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New Inorganic and Organometallic Heterocyclic Compounds Derived From Novel Heterodifunctional Phosphorus-Nitrogen Ligands

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NEW INORGANIC AND ORGANOMETALLIC HETEROCYCLIC COMPOUNDS DERIVED FROM NOVEL HETERODIFUNCTIONAL PHOSPHORUS-NITROGEN LIGANDS

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Abstract The first examples of phosphiniminatophosphanes, $\text{Me}_3\text{SiN}=\text{P}(\text{Ph}_2)(\text{CH}_2)_n\text{P}(\text{Ph}_2)$, were prepared from the reactions of the diphosphanes, $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ [$n = 1$ and 2], with N_3SiMe_3 . ARPHOS, $\text{Ph}_2\text{As}(\text{CH}_2)_2\text{PPh}_2$, is oxidized only at phosphorus to yield a new phosphiniminatoarsane. These new heterodifunctional ligands with both hard and soft centres react with metal compounds to yield chelates and metal-nitrogen bonded metallacycles. The Rh(I) carbonyl derivatives of these ligands convert methanol to acetic acid in the presence of CO and CH_3I . Re(VII) reacts with $\text{Ph}_2\text{PCH}_2(\text{Ph}_2)\text{P}=\text{NSiMe}_3$ to form a Re-N metallacycle. Alkyl and aryl germanium halides suffered germanotropic rearrangements and loss of organic substituents in reaction with the doubly oxidized diphosphane, $\text{Me}_3\text{SiN}=\text{P}(\text{Ph}_2)\text{CH}_2(\text{Ph}_2)\text{P}=\text{NSiMe}_3$, to form a new germanium spirocycle containing both Ge-C and Ge-N bonds. The isomeric spirocycle with only Ge-N bonds was also prepared from GeCl_4 and the bis(phosphiniminato)methane and from a germanium diazide and dppm. Structural confirmation of all of the new metallacyclic compounds was provided by complete ^1H , ^{13}C , ^{31}P and ^{29}Si NMR studies.

INTRODUCTION

The chemistry of heterocyclic compounds constructed with main-group element skeletons such as the phosphazenes, thiazenes or borazenes has received increased attention recently.¹ Incorporation of additional heteroatoms such as transition metals within cyclic frameworks has provided a new dimension to this area. In particular the main group

skeletons appear to be stabilized and yet also acquire markedly different reactivity.^{2,3}

Our interest has focussed on the design of heterobifunctional ligand systems which offer the potential for the preparation of metallic compounds with specific, useful reactivity (they may be useful catalysts) and possibly also heterobimetallic systems with similar potential. In this report we describe the behaviour of examples of such ligands based on phosphorus, nitrogen and, briefly, arsenic.

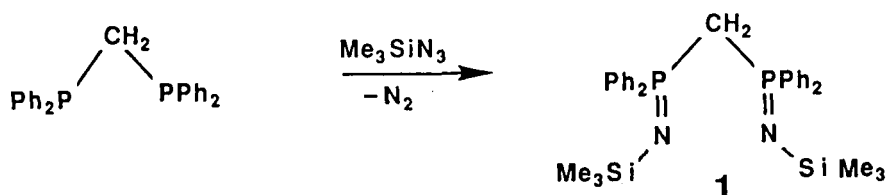
PREPARATION OF THE LIGANDS

Oxidation of phosphorus(III) centers with organic azides was described many years ago by Staudinger and Meyer⁴

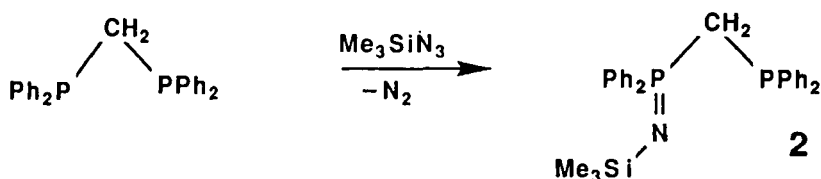


This reaction with the more versatile azide reagent, trimethylsilylazide,⁵ yields a functionalized phosphinimine, $R_3P=NSiMe_3$, which may undergo further reactions.⁶

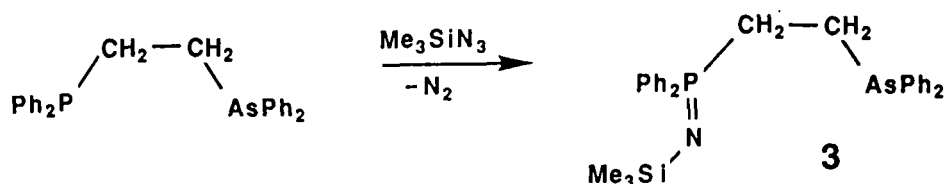
Although the more usual reaction of a bridged diphosphane is the oxidation of both phosphorus atoms:⁷



a simple modification of the experimental procedure yields efficient production (nearly quantitative) of the compound oxidized at only one phosphorus centre to form the interesting heterodifunctional ligand 2.



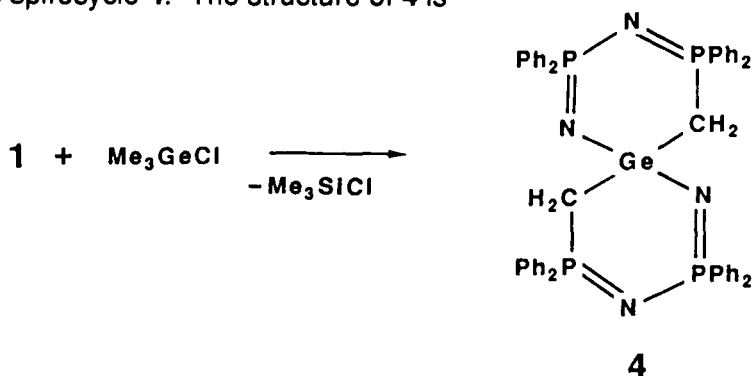
The arsenic-phosphorus compound ARPHOS reacts exclusively at phosphorus to produce another heterodifunctional ligand; in this case the phosphiniminatoarsane, **3**, which also has interesting ligating properties.



Although in this work we focus on the singly oxidized methylene bridged derivative **2** and related chemistry of **3** in order to explore the chemistry of ligand systems with heterodifunctional character, in particular those cases which lead to metallacyclic rings containing a metal-nitrogen σ bond, one example of interest derives from the chemistry of the doubly oxidized phosphorus system **1** with germanium.

SPIROCYCLIC GERMANIUM RINGS

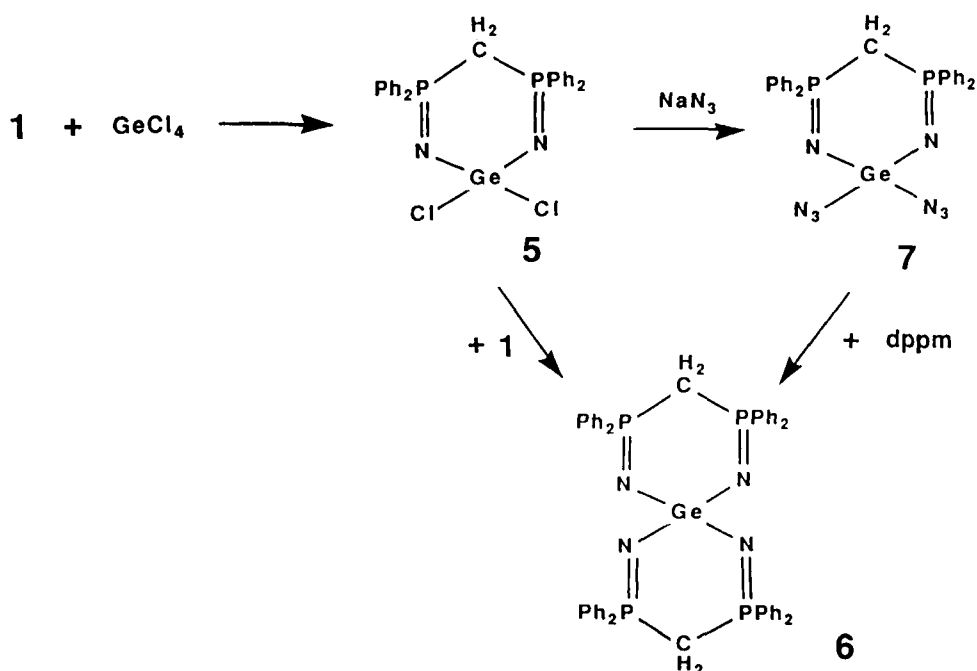
Our first example of new spirocyclic rings arose from an attempt to transmetallate **1**. Me_3GeCl reacted with **1** to form a totally unexpected symmetric spirocyclic **4**. The structure of **4** is



clearly demonstrated by the AB spin system in the ^{31}P NMR spectrum which shows that there are two different but formally pentavalent phosphorus atoms. Selective decoupling of ^{31}P in the ^1H NMR spectrum

showed that the methylene protons were coupled to only one of the phosphorus atoms, consistent with the structure shown. Carbon-13 NMR spectroscopy further demonstrated that there are two sets of chemically distinct aryl rings with small differences in ortho, meta and para carbon signals and larger differences in the ipso carbon signals. The latter show two distinct couplings to phosphorus. Triphenylgermane gave the same product indicating that the CH_2 bridge between Ge and P is not formed via deprotonation of methyl groups but rather that complete removal of aryl or alkyl substituents from Ge has occurred.

The isomeric spirocycle **6** could be easily synthesised from GeCl_4 and **1**. We proceeded in two steps, although it was not necessary to do so, and we isolated and characterizing the expected intermediate **5**. This intermediate can also be converted to the diazogermane **7** [CAUTION] which was then treated with bis(diphenylphosphino)methane (dppm) to yield the symmetric spirocycle **6** in a Staudinger type reaction:

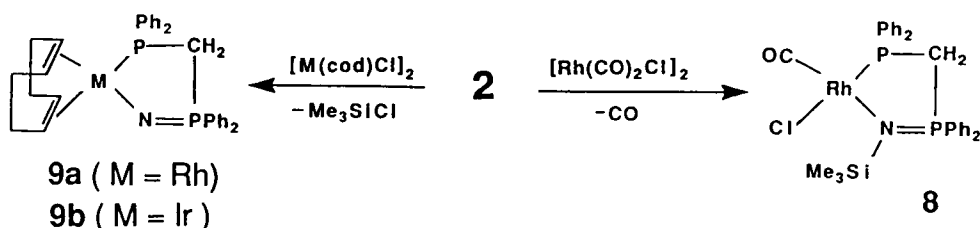


Two routes to **6** were therefore demonstrated. Compound **6** is however spectroscopically uninteresting showing only a single ^{31}P NMR signal as

the result of totally equivalent phosphorus atoms and has no unusual temperature dependence in the nmr spectra.

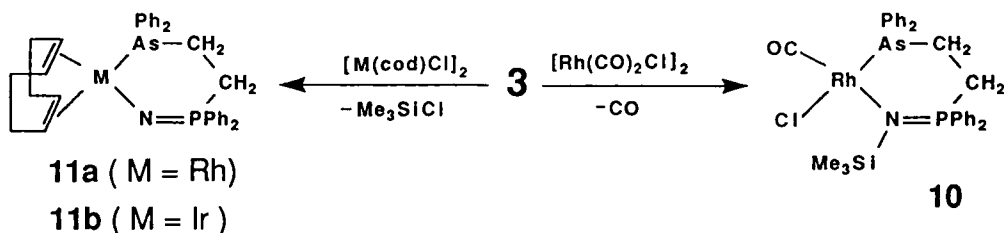
LOW OXIDATION STATE RHODIUM(I) METALLACYCLES

The reactions of Rh(I) complexes with the monooxidized phosphiniminato-phosphane **2** show an interesting contrast with two modes of reaction. $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ reacts with **2** to form the square planar chelate **8**. The ligand here acts simply as a bidentate Lewis base. With



$[\text{Rh}(\text{cod})\text{Cl}]_2$ (cod = cyclooctadiene) however, Me_3SiCl is eliminated and a Rh-N σ bond is formed in the metallacycle **9a**. The most remarkable feature of the compound **9a** is the very low field ^{31}P NMR shift of the phosphazene phosphorus relative to the value in the parent compound. This low field shift may be indicative of some delocalization in the ring system. $[\text{Ir}(\text{cod})\text{Cl}]_2$ reacts with **2** in a similar fashion to the Rh(I) complex to form the Ir analog **9b**. The same shift to low field of the phosphazene phosphorus signal was observed illustrating the general nmr characteristics of this structural feature.

Parallel chemistry was demonstrated by the phosphiniminatoarsane **3**. $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ forms the chelate complex **10** and $[\text{Rh}(\text{cod})\text{Cl}]_2$ or $[\text{Ir}(\text{cod})\text{Cl}]_2$ form the metal-nitrogen metallacycles **11**.

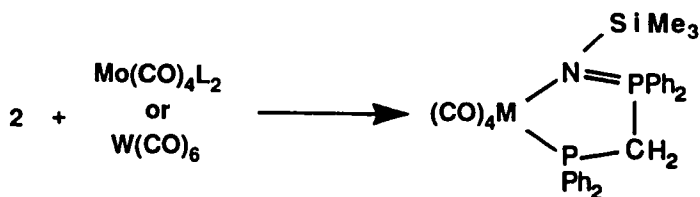


The difference in reactivity shown by the carbonyl and cod complexes can be rationalized in terms of the character of the substituents on the metal. We presume that the initial step is phosphane (or arsane) coordination of the ligand with concomitant formation of the monomeric complex. In the case of the CO complexes, CO is easily lost and the nitrogen base coordinates to form the chelate. Although we have evidence that this reaction is reversible, the CO concentration under normal reaction conditions is low, hence the next step, the elimination of Me_3SiCl which would give a 14 electron species, does not proceed because insufficient CO is available to provide the necessary additional electron donor to create a stable 16 electron species. In contrast the cod system can proceed *via* coordination of the nitrogen base with the cod becoming a 2 electron donor followed by elimination of Me_3SiCl and the reestablishment of the 4 electron donor contribution of cod to produce a stable 16 electron species.

Preliminary experiments with the Rh chloro carbonyl derivatives **8** and **10** show that a 1:1 mixture of either of these complexes with CH_3I converts methanol to acetic acid in the presence of CO. Further tests of the catalytic activity of these complexes are under way.

METALLACYCLES CONTAINING Mo(0) AND W(0)

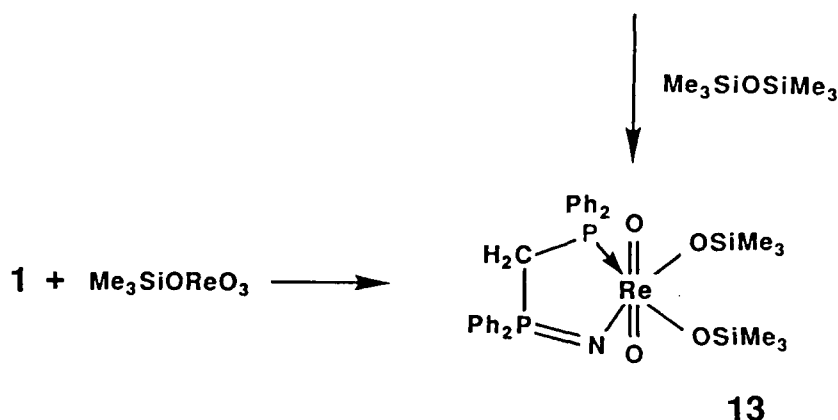
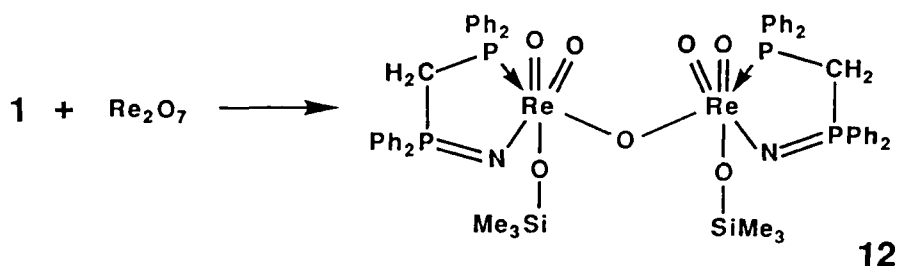
Direct reaction of $\text{W}(\text{CO})_6$ with the phosphiniminatophosphane in refluxing acetonitrile yields the W(0) derivative. The corresponding isoelectronic Mo(0) metallacycle was similarly prepared from **2** and



$\text{Mo}(\text{CO})_4(\text{Pip})$ (Pip = piperidine). These new metallacyclic compounds are air stable crystalline solids in which the carbonyl groups have a *cis* disposition around the metal centers.

HIGH OXIDATION STATE METALLACYCLES

The migration of SiMe_3 groups to oxygen atoms of high valent metal oxides provides a smooth route to the formation of metallacycles of these high oxidation state metals. This transformation is demonstrated by the reaction of Re_2O_7 with **2**:



The product **12**, is formulated as a μ -oxo bridge dirhenium species. We have not completely determined the structure of **12** but hexamethyldisiloxane converts **12** to the monomeric species **13**. Direct synthesis of **13** results when $\text{O}_3\text{ReOSiMe}_3$ ⁸ is treated with **2**. The structure proposed for **13** in which OSiMe_3 groups are *cis* to each other is strongly suggested by the two distinct signals observed (at 17.2 and 7.5 ppm) in the ^{29}Si (INEPT) nmr spectrum. We prefer the alternative with the *trans* dioxo structure because the difference in ^{29}Si NMR shifts is relatively small, but we cannot rule out the alternative arrangements with a *cis* dioxo structure.

Both high and low oxidation state metals react cleanly with our heterobifunctional ligands forming in several cases novel metal-nitrogen bonded systems in a metallacycle. This heterodifunctionality at the metal centres subsequently introduces differences in reactivity which may ultimately yield catalytically useful systems. Work is proceeding along these lines.

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