

SYNTHESIS AND STRUCTURE OF SOME NEW ORGANOPHOSPHORUS LI- GANDS AND THEIR METAL COMPLEXES

Hubert Schmidbaur

Anorganisch-chemisches Institut der Technischen Universi-
tät München, Lichtenbergstr. 4, 8046 Garching,
West Germany

Abstract - Following a brief introduction into the coordination chemistry of phosphorus ylides, some new examples of complexes with catalytically active metals are presented. Mononuclear derivatives of platinum, iridium, palladium, rhodium, and nickel were synthesized from salt-free (or lithiated ylides) and the metal halides and their phosphane or olefine adducts. Both ionic and non-ionic species could be isolated and characterized by analytical and spectroscopic techniques. Titanium forms predominantly binuclear compounds. Novel coordination compounds of the alkaline metals were obtained with phosphanoalkyl benzyldiene phosphoranes. In a crystal structure analysis a discrete phosphane-sodium donor interaction and a polyhapto coordination of the metal to the benzyldiene function were detected. Mixed complexes of phosphonium-bis-methylide and bis-phosphano-methanide ligands were also investigated by x-ray diffraction in order to elucidate the structure of the latter system. The ligand was found to form a planar four-membered chelate ring with a symmetrical P-C-P moiety, characterized by strong ylidic π -bonding.

INTRODUCTION

Phosphorus ylides are now well known to be extremely powerful donors and to form complexes with virtually every metal of the Periodic Table 1,2). Examples documented in the literature range from lithium 3) to uranium 4), including even the rare earth 5), functioning as coordination centers for the ylidic carbanions.

These complexes are true σ -organometallic compounds, which often exhibit surprisingly high thermal and chemical stability, due to the influence of the phosphonium cation in the α -position relative to the metal.

Recent activities in this laboratory have concentrated on complexes of the catalytically active metals of Group VIII. Ylides with bulky substituents have been designed, which should allow the synthesis of mononuclear species as described previously 2), whereas with small substituents polynuclear systems are known to prevail 6-9). This is again confirmed in the results with titanium(IV) where a few binuclear compounds could be prepared.

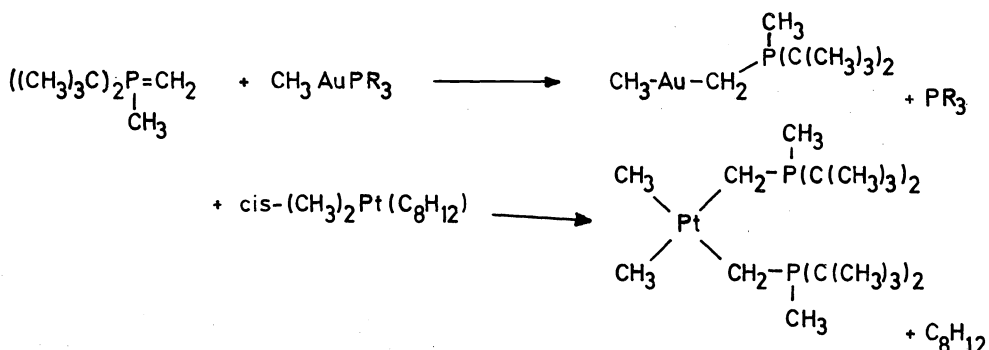
As already mentioned it has been well known that lithium - and in special cases sodium - are sometimes strongly coordinated to ylides, but none of the resulting complexes has been structurally characterized. As part of a continuing program a series of such alkaline metal complexes with special combinations of substituents has been synthesized and subjected to an x-ray diffraction analysis, which can provide first information on the nature of the alkali-ylide interaction. Many reactions in organic synthesis strongly depend on the nature and the concentration of alkali halide present in the system and thus a knowledge of the interaction is of great general importance.

Issleib and collaborators 10) have first reported on the formation and the coordination chemistry of bis-phosphano-methanide $[\text{R}_2\text{PCHPR}_2]^-$ ligands, which are closely related to the classical ylides or ylide anions. In synthetic and structural work they were now shown to provide a novel coordination geometry quite distinguished from the well-known diphosphanomethane ligands.

NEW TRIALKYLPHOSPHONIUM METHYLIDE AND DIALKYLPHOSPHONIUM-BIS-METHYLIDE COMPLEXES

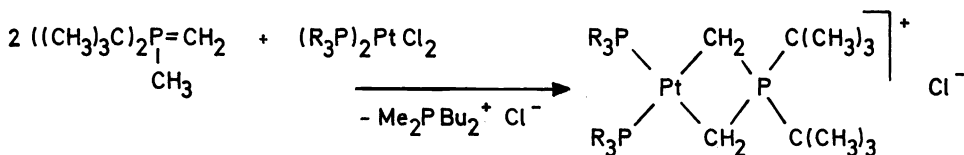
(G. Blaschke, W. Scharf) *

Ylides with two or three tert.-butyl groups were shown to be unstable and prone to undergo reductive elimination of isobutene 11). They can be stabilized by engaging their carbanionic function in bonding to acceptor partners. This reaction can be used to synthesize the corresponding complexes of gold and platinum according to the following equations:

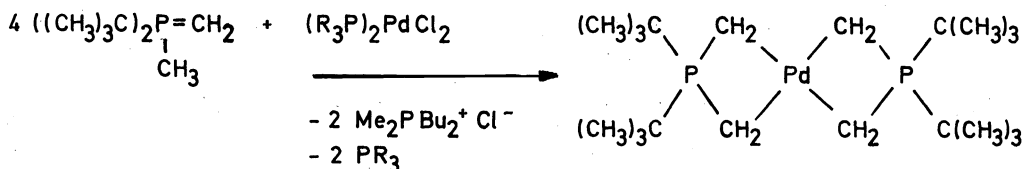


The products are colourless airstable materials, with a linear or square-planar array of ligands, respectively. The central atom is bonded solely to saturated carbon atoms in both cases. This situation is only duplicated in the anions $[\text{R}_2\text{Au}]^-$ and $[\text{R}_4\text{Pt}]^{2-}$ as described by Tobias 12) and Kochi 13). $(\text{CH}_3)_3\text{P=CH}_2$ gives the same reaction 14).

With $[(\text{CH}_3)_3\text{P}]_2\text{PtCl}_2$ a cationic species is generated, in which the two phosphanes are retained in the coordination sphere:



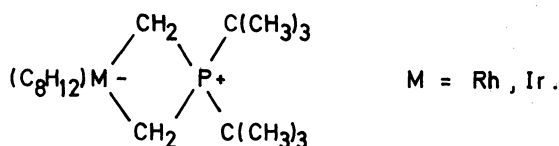
The reaction with the corresponding nickel and palladium complexes leads to a symmetrical bis-chelate product with complete displacement of the phosphanes under similar conditions:



Ni ~ Pd

The monomeric complexes differ markedly from the oligomers obtained with $(\text{CH}_3)_2\text{P}=\text{CH}_2$ (15). The analogous Pt compound could only be synthesized via the lithiated ylide.

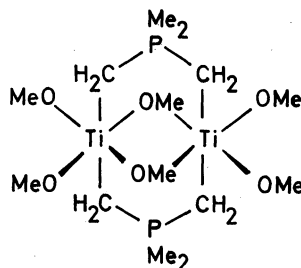
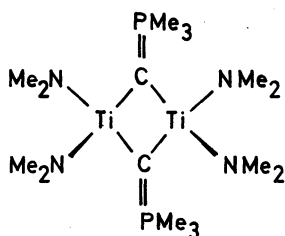
Iridium and rhodium derivatives of a similar nature were prepared from 1,5-cyclooctadiene metal halides and $t\text{-Bu}_2\text{MeP}=\text{CH}_2$. Again an equivalent of phosphonium salt is formed as a by-product of the trans-ylidation:



The olefinic ligand in these compounds can be displaced by stronger donors like phosphanes, carbon monoxide etc. In previous work by Grey et al. with $(\text{CH}_3)_2\text{P}=\text{CH}_2$ it could be demonstrated, that homologous monomers are in equilibrium with oligomers (16) and thermodynamic data are available for the conversion (17).

The reaction of ylides with titanium halides is extremely complicated and no definite statements can be made to date about the course of the process and the nature of the products. It was only with bis-cyclopentadienyl-titanium(III) halides, that well-characterized products were isolated (18,19), which were of the expected configuration.

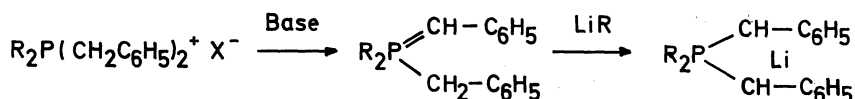
From alkoxo- and amino-titanium(IV) halides, however, two new types of complexes could be prepared, the structure of which is shown in the two following drawings. The alkoxo and ylide bridged dimer was subjected to a successful x-ray diffraction analysis (20). The amino compound contains the titanium atoms as substituents to the ylidic carbon and is thus analogous to many well-known silicon, germanium or tin derivatives (1).



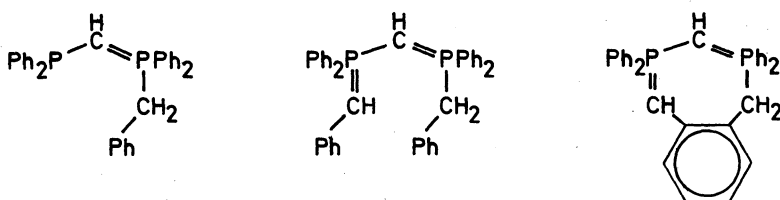
YLIDE COMPLEXES OF ALKALINE METALS

(U. Deschler, Th. Costa)

Dialkyl(benzyl)benzylidenephosphoranes were found to undergo a reaction with one equivalent of an alkyllithium component to form a lithium phosphonium-bis-benzylide according to the following equation:

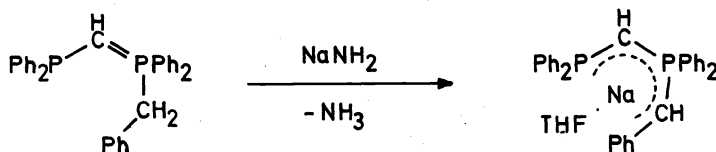


R = alkyl, aryl.



It is assumed that the interaction of the metal with the difunctional ylide is of a similar nature as in the sodium complexes below. The compounds are extremely strong bases.

A crystalline sodium complex was synthesized from the ylide $\text{Ph}_2\text{PCHPPh}_2\text{CH}_2\text{Ph}$ (or its phosphonium salt precursor) and NaNH_2 or NaH in an ether solvent:

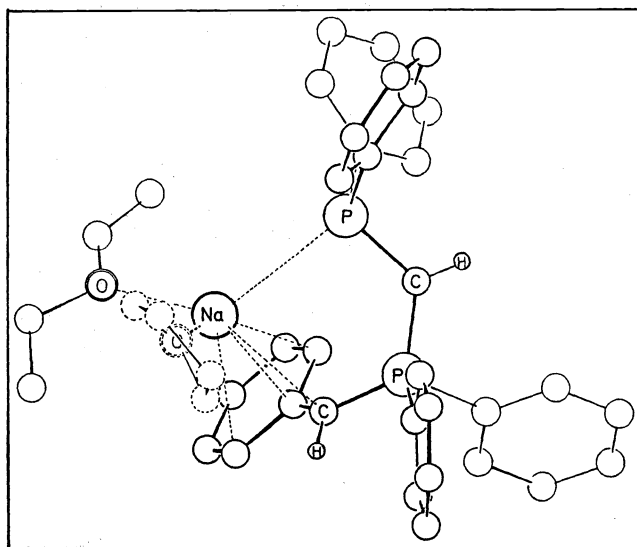


Ph = Phenyl.

Its novel structure could be elucidated by x-ray crystallography and the result is shown in the figure. The ylidic ligand is attached to the metal through a $\text{P} \rightarrow \text{Na}$ donor bond and through a Na -benzylidene interaction. The latter appears to result from electrostatic forces between Na^+ and the negative charges at the benzylidene- and the ortho-carbon atoms as expected from the classical charge distributions in a benzylidene anion. A molecule of diethylether and a molecule of tetrahydrofuran complete the coordination sphere of the metal.

Figure

Molecular Structure of
 $\text{Ph}_2\text{PCHPPh}_2\text{CHPh Na} \cdot \text{THF} \cdot$
 Et_2O

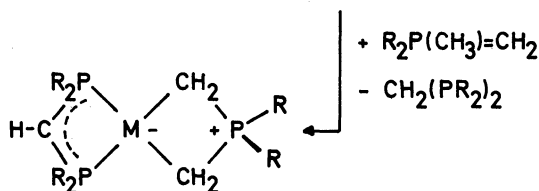
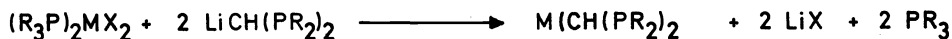


Related compounds are derived from difunctional non-cyclic and cyclic benzylidene ylides, which have recently been synthesized. Their structure is expected to be of a similar type, but no details are available as yet. Potassium forms analogous complexes and it is expected, that for most of the alkaline and earth alkaline metals specific ligand systems can be designed, which provide a suitable array of carbanionic donor sites.

BIS-PHOSPHANO-METHANIDE COMPLEXES

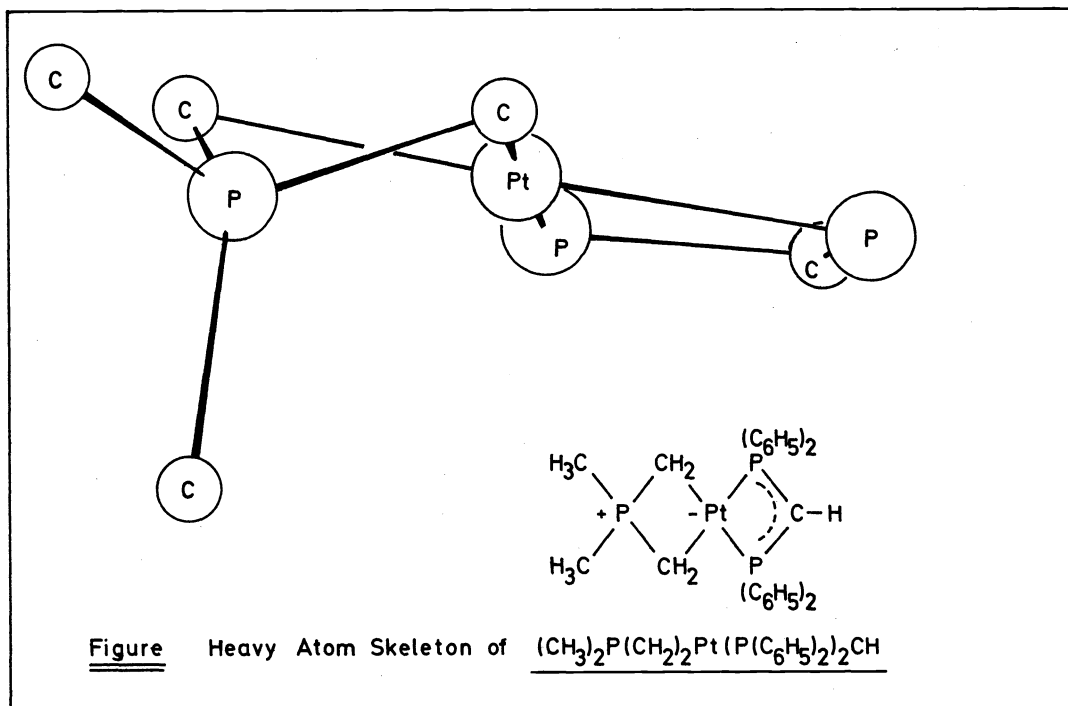
(J.M. Bassett, J.R. Mandl)

Bis-phosphano-methanes $R_2PCH_2PR_2$ are known to form a large variety of metal complexes, including some recent examples of platinum and the coinage metals, e.g. 21). Only in very few cases, however, the corresponding anions have been introduced as ligands. The products obtained in this earlier work were mostly insoluble and characterization of the materials proved very difficult. It has now been found that a combination of $R_2PCHPR_2^-$ anions and ylide ligands $CH_2PR_2CH_2^-$ yields well-defined soluble and crystalline complexes of the following types 22):



M = Ni, Pd, Pt.

Of the latter class the platinum complex was analyzed by x-ray diffraction. It exhibits an interesting structure with a folded ylidic four-membered ring and a planar bis-phosphano-methanide four-membered ring. These structural features differ markedly from those of the corresponding bis-phosphano-methane complexes, which are known to have the folded envelope conformation. It can be envisaged that there should exist a whole range of bis-phosphano-methanide complexes with quite different chemical behaviour from that of the parent $R_2PCH_2PR_2$ compounds.



$R_2PCHPR_2^-$ complexes may also be viewed as ylidic species with the metal atoms as true substituents to the phosphonium center. Thus a close relation to ylides and their complexes becomes evident, which should prove useful in further systematic studies.

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