

CLASSICAL AND NOVEL YLIDE SYSTEMS IN ORGANOMETALLIC CHEMISTRY

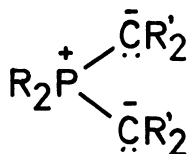
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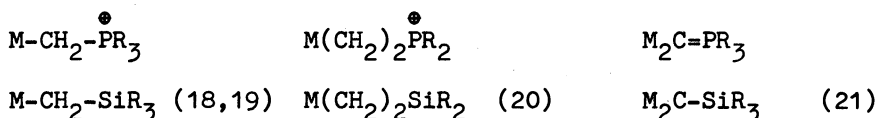
Abstract - Ylide-based organometallic compounds have become an active research topic in several academic and industrial institutions. After a short literature account this article reflects the recent progress made in the author's laboratory, the main attention being focussed on the chemistry of phosphorus ylides with bulky substituents, of unstrained or strained cyclic ylides, and of polyfunctional ylidic systems. Ylide complexes of a series of main group and transition metals have been obtained and characterized by spectroscopic and x-ray techniques. The examples of representative molecules range from volatile magnesium and mercury phosphoniummethylides via titanium(III) and -(IV) metallocycles to gold(I) macrocycles. In combination with the formally related diphosphinmethanide ligand, ylides form very stable mono- and binuclear products with symmetrical structures. The phosphametallocycles of these species are related to allyl-metal as well as to metallocyclobutane systems.

INTRODUCTION

From recent work in various laboratories it has become apparent, that ylides of phosphorus and related elements are extremely powerful ligands to both main group and transition metals. A rapidly growing new class of organometallic compounds has emerged, initially started with the classical monofunctional ylides of the types $R_3P=CH_2$, $R_2As=CH_2$ or $R_2S(O)=CH_2$. This earlier work is already well documented (1-17), but many new and interesting aspects have recently been found to arise from a study of the rôle of ylides with strong steric hindrance, with strained or unstrained ring systems, with multiple functionality - either conjugated, cumulated or bis-terminal -, and with the novel phosphonium-bis-methylide/diphosphinmethanide ligand combination. These results are presented here in the form of a short account of the author's investigations during the last three years. The reader is directed to some of the leading references in the appendix for information on the many important contributions



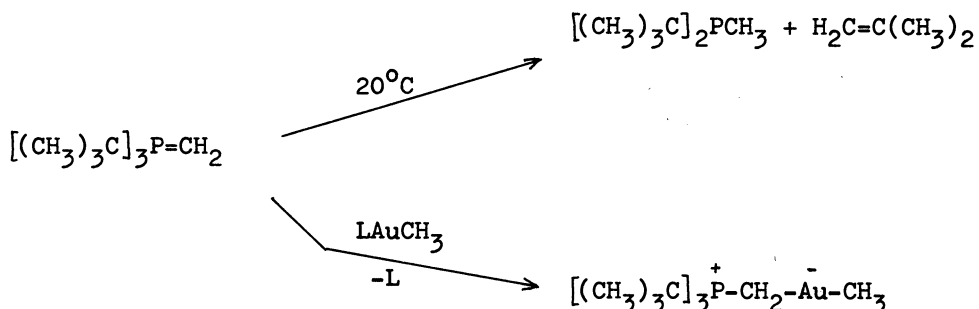
from other workers. A significant part of this research has been stimulated by evidence for potential applications of ylide complexes in catalysis and, to a minor extent, in pharmacology. There are also meaningful parallels to some of the well-known organometallic chemistry of silylmethyl and related compounds, (18,19) that have become important model compounds for a study of metal-to-carbon σ bonds:



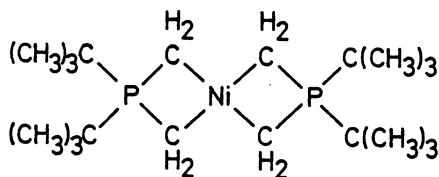
Tert.-butyl-methylene-phosphoranes. (G. Blaschke) (22)

In a search for phosphorus ylides with extremely bulky substituents, the triade of compounds $(\text{CH}_3)_n[(\text{CH}_3)_3\text{C}]_{3-n}\text{P}=\text{CH}_2$ was synthesized using standard reagents under mild conditions, liquid ammonia being the preferred solvent. The tris-tert-butyl compound was found to be thermally unstable, undergoing reductive elimination of isobutene, induced by the strong basicity of the ylidic carbanion in the crowded molecule. (This crowding also becomes evident from variable temperature ^{13}C -nmr spectroscopy, which reveals a hindered rotation about the P-C single bonds).

Coordination derivatives of this ylide, in which the ylidic function is no longer available, do not eliminate olefine, however, and are stable σ -organometallic compounds:



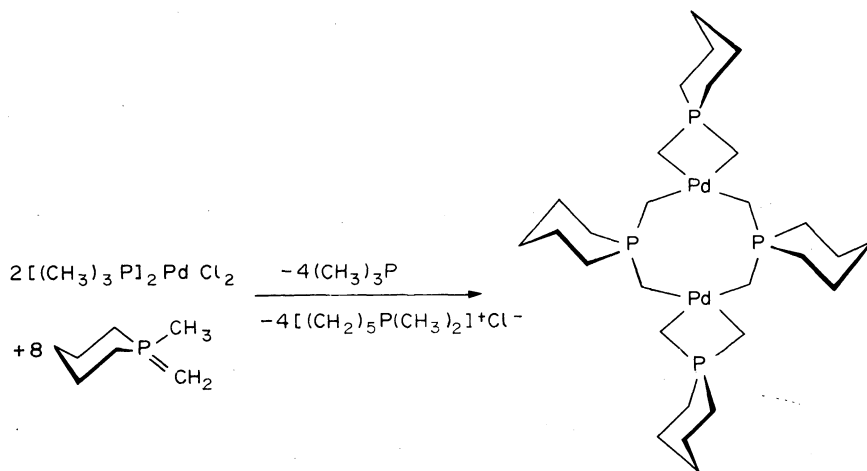
The comparatively small ylide $(\text{CH}_3)_3\text{P}=\text{CH}_2$ is known to form a complex variety of isomeric metal complexes, as e.g. in the $\text{NiCl}_2/(\text{CH}_3)_3\text{P}=\text{CH}_2$ system (23). In contrast, experiments with the bis-tert-butyl-ylide typically lead to a sole product, due to the steric requirements of the ligand:



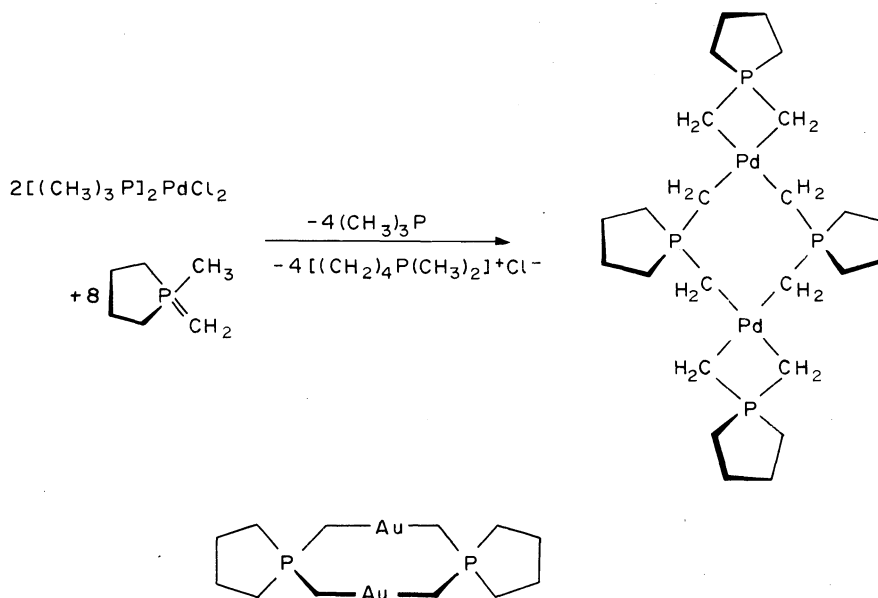
Similar results are obtained for the coinage metals, for palladium and platinum.

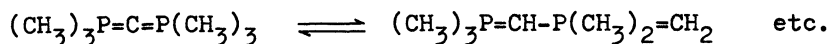
Phosphorinanium and Phospholanium Ylides (H.P. Scherm) (24)

Ylides become sterically much less demanding if their onium center is made an integral part of a heterocyclic system. For this purpose the six- and five-membered rings were chosen, for none of which ylides had been described in the literature. Whereas the phosphorinane ylide presented no synthetic problem and could be easily converted into very stable organometallic compounds with remarkable structures



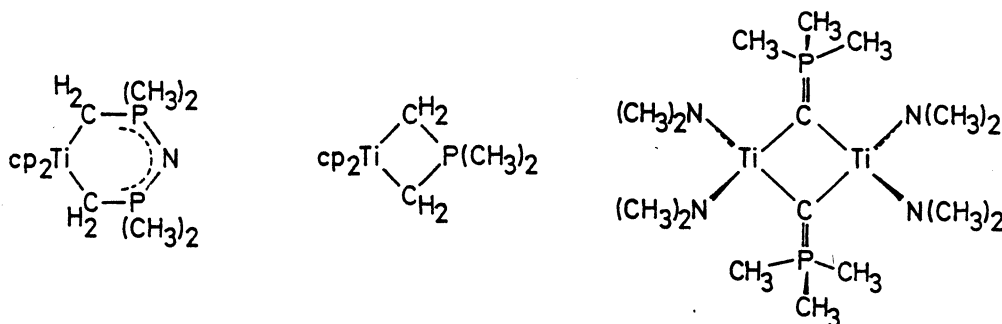
the phospholane homologue was shown to be unstable and undergo oligomerisation with ring cleavage. Again, however, its complexes do not exhibit such a rearrangement, because of the absence of the free ylidic function. One of these air-stable products was characterized by an x-ray structure determination:





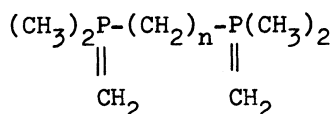
For the individual syntheses a series of reaction pathways has been developed, including metall halide, alkyl and amide precursors.

While bicyclopentadienyltitanium(III) halides also form the above cyclic ylide complexes, titanium(IV) amides give rise to novel products not previously observed with transition metals:



The titanium(III) species give very clear low-temperature ESR spectra, exhibiting a doublet (13,29) and triplet hyperfine splitting through the phosphorus nuclei, respectively.

Bis-terminal ylides of the general formula



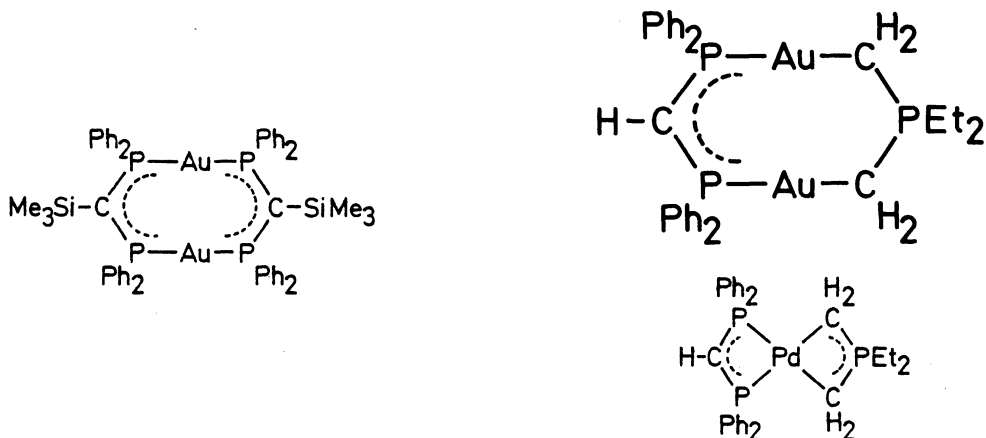
are another group of double ylides, for which quite distinguished donor properties are observed. Macrocyclic as well as polymeric materials have been obtained, as might be expected.

Phosphonium-bis-methylide/Bis-phosphino-methanide Complexes (J.R. Mandl, A. Wohlleben)

Current activities are also directed to novel combinations of ylidic and phosphinomethanide (35) ligands of the following type: (36)



Both triatomic donor moieties can be employed as chelating and bridging ligands to metals, as in the following mono- and binuclear species, where the CPC^o and PCP^o units are represented in the same molecule (37):



For the synthesis of these compounds the metal bis-diphenylphosphino-methanides are essential precursors. Introduction of a trimethylsilyl group at the bridging carbon is advantageous for the solubility properties of some of the products, thus permitting their spectroscopic characterization. ³¹P-NMR studies were of special significance for an elucidation of the highly symmetrical structures. Work with aminodiphosphine analogues is in progress.

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