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Preliminary communication

PENTAMETHYLCYCLOPENTADIENYL SUBSTITUTED DIPHOSPHENE, BICYCLO[1.1.0]TETRAPHOSPHANE, CYCLOTETRAPHOSPHANE AND CYCLOTRIPHOSPHANES FROM DIHALOGENO(PENTAMETHYLCYCLOPENTADIENYL)PHOSPHANES

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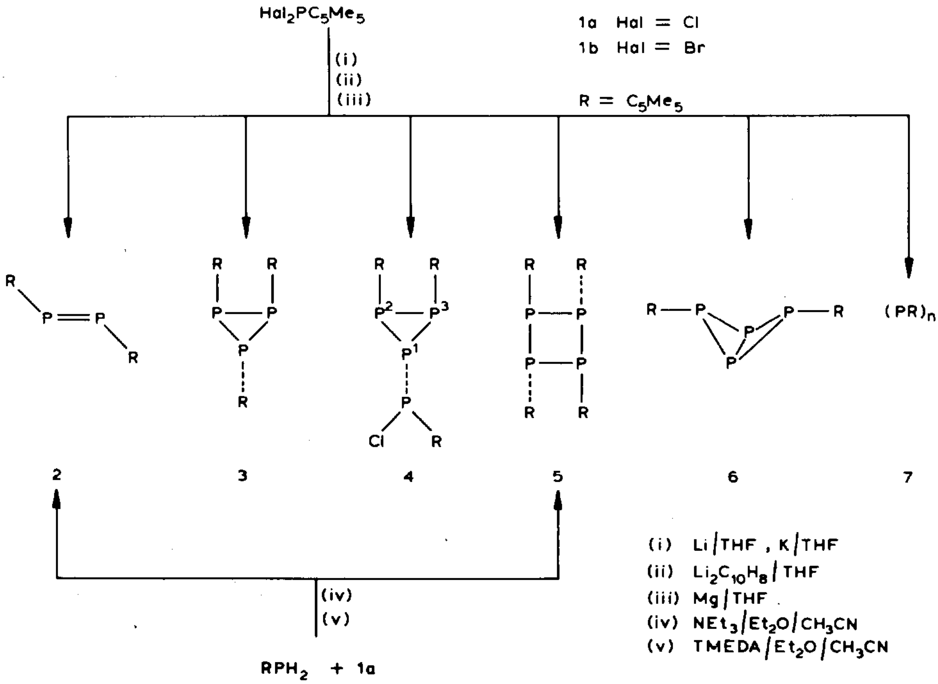
Summary

Reaction of dichloro- or dibromo-(pentamethylcyclopentadienyl)phosphane with Group I or Group II metals gives pentamethylcyclopentadienyl substituted diphosphene, bicyclo[1.1.0]tetraphosphane, cyclotetraphosphane and cyclotriphosphanes, which have been unambiguously characterised from their NMR data.

In phosphorus chemistry compounds involving $p\pi$—$p\pi$ bonds [1], such as diphosphenes, and strained small ring systems [2], such as are present in cyclotriphosphanes, are of considerable interest to both experimentalists and theoreticians. Some of these species have been synthesized using pathways starting from dihalogenophosphanes and alkyllithiums or Group I or Group II metals as reducing agents. We thus decided to explore the use of this type of reaction in our investigations of the chemistry of pentamethylcyclopentadienylphosphanes [3].

Reaction of dichloro- (**1a**) or dibromo-(pentamethylcyclopentadienyl)phosphane (**1b**) [3] with reducing agents such as lithium, lithium naphthanelide, potassium or magnesium in tetrahydrofuran (THF) between —80°C and room temperature proceeds exothermically to give a range of phosphorus-containing species (see Scheme 1). Most of the products have not been isolated in analytically pure form [4], but their structures have been unambiguously identified from their NMR spectra [5].

The only products observed in the reaction of **1b** with magnesium-powder or -turnings in THF are the diphosphene **2**, the bicyclo[1.1.0]tetraphosphane **6**, and the cyclotriphosphane **3**. Compound **3** was obtained by dissolving the $MgBr_2$-free crude product in acetonitrile and precipitation of **3** by addition of



SCHEME 1

diethyl ether. The ^{31}P NMR spectrum of 3 consists of a doublet and a triplet centered at −89.3 and −125.3 ppm, respectively, with a ^{1}J(PP) coupling constant of 213 Hz. These data are in agreement with those observed for other cyclotriphosphanes [2] (e.g. (^{t}BuP)$_3$: −71.9 and −108.1 ppm; ^{1}J(PP) −201 Hz [6]). ^{1}H and ^{13}C NMR spectra of 3 reveal no fluxional behaviour for this pentamethylcyclopentadienyl compound (δ(^{1}H): allylic-CH$_3$: 1.08 (3H, d, ^{3}J(PH) 7.4 Hz); 1.16 (6H, dd, J(PH) 6.0 Hz, J(PH) 6.8 Hz); vinylic-CH$_3$: 1.67 (6H), 1.72 (6H), 1.83 (6H), 1.93 (6H), 2.03 (6H); 2.18 (6H), δ(^{13}C): C-CH$_3$: 11.2, 11.3, 11.6, 11.8, 11.9; C(1) ring 59.1—60.1; C(2), C(3), C(4), C(5) ring: 135.1, 135.6, 139.4, 140.6, 142.1)

The ^{31}P-NMR-chemical shift of the diphosphene 2 is +504.0 ppm, which is in agreement with chemical shifts observed in other P=P double-bond systems (e.g. bis[(2,4,6-tri-t-butyl)phenyl]diphosphene: δ(^{31}P) +494 ppm [7]).

The ^{31}P NMR spectrum of the bicyclo[1.1.0]tetraphosphane (6) shows characteristic highfield signals with triplet structures centered at −133.6 ppm for the phosphorus atoms bearing the pentamethylcyclopentadienyl ring and −357.3 ppm for the bridge-head phosphorus atoms; the observed ^{1}J(PP) coupling constant is 194 Hz. These data are comparable to those obtained for the bis[bis(trimethylsilyl)amino]bicyclo[1.1.0]tetraphosphane. (δ(^{31}P): −79.1 and −287.3 ppm; ^{1}J(PP) −225 Hz; for the isomer with both amino-groups in an "equatorial" position [8]).

The reactions of 1a with lithium, lithium naphthanelide, potassium or magnesium turnings or powder in THF at various temperatures gave the cyclotriphosphane (3), the bicyclotetraphosphane (6), the cyclotetraphosphane (5) and the 1-[chloro(pentamethylcyclopentadienyl)phosphino]-2,3-bis(pentamethylcyclopentadienyl)cyclotriphosphane (4) along with varying amounts of unidentified polyphosphanes (7). The ^{31}P NMR spectrum of 5 shows a singlet at $\delta(^{31}P)$ −41.5 ppm, which is comparable with the ^{31}P shift of tetra-t-butylcyclotetraphosphane [9] ($\delta(^{31}P)$ −57.1 ppm).

The ^{31}P NMR spectrum of 4 was analysed by ^{31}P—^{31}P-2D-shift-correlated-spectroscopy (COSY). The compound gives raise to three signals in a ratio of 1/2/1, centered at +8.3, −114.4, and −140.7 ppm, respectively. The "doublet" centered at +8.3 ppm ($^1J(PP)$ 296 Hz, $^2J(PP)$ 20 Hz) is assigned to the exocyclic phosphino group, the "doublet" centered at −114.4 ppm to the phosphorus atoms 2 and 3 with $^1J(PP(1))$ 209 Hz; the "doublet of triplets" for P(1) is centered at −140.7 ppm. Although the phosphino group is a center of asymmetry (thus P(2) and P(3) should give raise to two different signals with a $^1J(PP)$ coupling constant between that for P(2) and P(3)), P(2) and P(3) have the same chemical shift. Structural analogous compounds have been synthesized with comparable chemical shifts and coupling constants, e.g. $(Me_3Si)(Me_3C)P_3(P(SiMe_3)_2)$ [10]. An additional ^{31}P NMR signal at +164.5 ppm present in the reaction mixture is assigned to pentamethylphosphabenzene, which has not yet further been characterised.

The diphosphene 2 and the cyclotetraphosphane (5) can be synthesized independently by the reaction of pentamethylcyclopentadienylphosphane [3] with 1a in a 1/1 mixture of diethyl ether and acetonitrile in the presence of triethylamine or *N,N,N',N'*-tetramethylethylenediamine at −20°C.

Two further important properties of the pentamethylcyclopentadienyl (pcp) ligand when connected to a phosphorus atom are obvious from the results. Firstly the pcp ligand can act as a leaving group in the reaction with Group I or Group II metals, secondly it must be regarded as a bulky ligand, suitable for stabilization of kinetically unstable compounds.

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References and Notes

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