SYNTHESIS AND CHARACTERIZATION OF BIS(PHOSPHINOMETHYL)-MAGNESIUM COMPOUNDS – STRUCTURE OF $[\text{Mg}(\text{CH}_2\text{PPh}_2)_2(\text{tmeda})]\cdot 2\text{Et}_2\text{O}$

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Tmeda adducts of phosphinomethyl lithium compounds $[\{\text{LiCH}_2\text{PR}_2(\text{tmeda})\}_2]$ ($\text{R} = \text{Me}, \text{Ph}$; $\text{tmeda} = N,N,N',N'$ -tetramethylethylenediamine) react with MgCl_2 in $\text{THF}/\text{Et}_2\text{O}$ yielding $\text{Mg}(\text{CH}_2\text{PMe}_2)_2\cdot 2\text{LiCl}$ **1a** and $[\text{Mg}(\text{CH}_2\text{PPh}_2)_2(\text{tmeda})]\cdot 2\text{Et}_2\text{O}$ **1b**, respectively. The two Et_2O molecules in **1b** are rapidly lost *in vacuo* yielding $[\text{Mg}(\text{CH}_2\text{PPh}_2)_2(\text{tmeda})]$ **1b'**. The identities of compounds **1** were confirmed by microanalysis and NMR spectroscopy (^1H , ^{13}C , ^{31}P). As shown by X-ray diffraction analysis, compound **1b** crystallizes as a monomer with crystallographically imposed C_2 symmetry. The magnesium environment is distorted tetrahedral with a primary donor set made up by two nitrogen atoms of the tmeda ligand and two carbon atoms of the η^1 -coordinated Ph_2PCH_2 ligands. The $\text{P}-\text{CH}_2$ bonds are shortened due to stabilization of the carbanionoid C atom by phosphorus. There are no unusual short interactions between the magnesium complex and the Et_2O molecules of crystallization.

INTRODUCTION

Main-group organometallics of the type $\text{L}_n\text{M}-\text{CH}_2\text{YR}_n$ ($\text{Y} = \text{heteroatom}$, $\text{R} = \text{alkyl, aryl}$, H , $\text{L} = \text{ligand}$) with Lewis-basic heteroatomic centers ($\text{YR}_n = \text{NR}_2, \text{PR}_2, \text{OR}, \text{SR}, \text{F}, \text{Cl}, \dots$) exhibit a great diversity of structures (e.g. η^2 -($\kappa^2\text{C,Y}$) coordination). Because of the Lewis-basic heteroatoms they are highly reactive in many cases, opening the possibility of entirely new reactions. Thus, carbenoid reactivity of halo- and oxymethyl lithium and Grignard compounds has been known for more than 30 years ago^{1,2} but that of the thiomethyl compound $[\text{LiCH}_2\text{SPh}(\text{pmdta})]$ ($\text{pmdta} = N,N,N',N'',N'''$ -pentamethyldiethylenetriamine) very recently.³

Phosphinomethyl lithium compounds LiCH_2PR_2 are well-known and proved to be typical bifunctional ambident compounds.⁴⁻⁷ Grignard compounds $\text{Mg}(\text{CH}_2\text{PR}_2)_2\text{X}^8$ and $\text{Mg}\{\text{CH}_2\text{P}(\text{O})\text{R}_2\}_2\text{X}^{9,10}$ were prepared in solution and $\text{Mg}\{\text{CH}_2\text{P}(\text{NSiMe}_3)_2\}_2\text{X}^{11}$ was even isolated as solid. It was also shown, that phosphorus ylides and double ylides can coordinate to magnesium.¹² Furthermore, the tetrakis(*P,P*-dimethylphosphinomethyl)magnesium complex $[\text{Li}(\text{tmeda})]_2[\text{Mg}(\text{CH}_2\text{PMe}_2)_4]$ has been prepared.¹³ The only compounds of the type $[\text{Mg}(\text{CH}_2\text{YR}_n)_2]$ with Lewis-basic heteroatoms isolated so far are those with $\text{YR}_n = \text{SPh}, \text{SMe}$.¹⁴ Carbenoids of the type $\text{Mg}(\text{CHRX})_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$; $\text{R} = \text{alkyl}$) were characterized by NMR spectroscopy.¹⁵

Here we report synthesis and characterization of bis(phosphinomethyl)magnesium compounds as well as the structure of bis(*P,P*-diphenylphosphinomethyl)(*N,N,N',N'*-tetramethylethylenediamine)magnesium-bis(diethyl ether) solvate.

MATERIALS AND METHODS

All reactions and manipulations were carried out under purified argon using standard Schlenk techniques and a glove box from Fa. MB Braun. *n*-Hexane, tmeda and $[\text{D}_8]\text{THF}$ were dried with LiAlH_4 . THF and diethyl ether were distilled from sodium benzophenone ketyl. NMR spectra were recorded on a Gemini 200 spectrometer (Varian) using the protio impurities and ^{13}C resonances of the deuterated solvents as references for ^1H and ^{13}C NMR spectroscopy, respectively. $\delta(^{31}\text{P})$ is relative to external H_3PO_4 (85 %). Microanalyses (C, H, N) were obtained from the microanalytical laboratory of the Department of Chemistry. Compounds $[\{\text{LiCH}_2\text{PR}_2(\text{tmeda})\}_2]$ ($\text{R} = \text{Me}, \text{Ph}$) were prepared according to the literature.^{16,17} MgCl_2 was commercially available (Merck).

Synthesis of $\text{Mg}(\text{CH}_2\text{PMe}_2)_2\cdot 2\text{LiCl}$ **1a**

At -78°C , $[\{\text{LiCH}_2\text{PMe}_2(\text{tmeda})\}_2]$ (892 mg, 2.25 mmol) and MgCl_2 (214 mg, 2.25 mmol) were dissolved in THF (10 ml) and stirred for 1 h yielding a cloudy solution. After stirring overnight at room temperature a clear solution was obtained. Half of the THF was removed *in vacuo* and diethyl ether (50 ml) was added. The colorless precipitate of **1a** was filtered, washed with hexane and dried *in vacuo* (Yield: 470 mg, 81 %).

C, 27.80; H, 6.22. Found: C, 26.91; H, 5.98. ^1H NMR (200 MHz, $[\text{D}_8]\text{THF}$): δ -0.60 (d, 4H, $^2J(\text{P},\text{H}) = 2.15$ Hz, CH_2), 0.90 ppm (s, 12H, CH_3). ^{13}C NMR (50 MHz, $[\text{D}_8]\text{THF}$): δ 10.3 (d, $^1J(\text{P},\text{C}) = 28.0$ Hz, CH_2), 22.6 ppm (s, CH_3). ^{31}P NMR (81 MHz, $[\text{D}_8]\text{THF}$): δ -38.7 ppm.

Synthesis of $[\text{Mg}(\text{CH}_2\text{PPh}_2)_2(\text{tmeda})]\cdot 2\text{Et}_2\text{O}$ **1b** and $[\text{Mg}(\text{CH}_2\text{PPh}_2)_2(\text{tmeda})]$ **1b'**

As described for **1a**, a solution of $[\text{Mg}(\text{CH}_2\text{PPh}_2)_2(\text{tmeda})]$ in THF was prepared from $[\{\text{LiCH}_2\text{PPh}_2(\text{tmeda})\}_2]$ (1.451 g, 2.25 mmol) and MgCl_2 (214 mg, 2.25 mmol). After removing the half of the THF *in vacuo*, diethyl ether (1–2 ml) was added. At -40°C , **1b** crystallizes in well shaped colorless

crystals that were suitable for X-ray crystallography. The crystals were filtered, washed with hexane and dried in vacuo yielding **1b'** (Yield: 1.10 g, 91 %).

1b': C, 71.32; H, 7.48; N, 5.20. Found: C, 69.78; H, 7.28; N 5.05. ^1H NMR (200 MHz, $[\text{D}_8]\text{THF}$): δ 0.02 (s, 4H, CH_2P), 2.12 (s, 12H, $\text{N}(\text{CH}_3)_2$), 2.36 (s, 4H, CH_2N), 7.09–7.56 ppm (m, 20 H, C_6H_5). ^{13}C NMR (50 MHz, $[\text{D}_8]\text{THF}$): δ 3.1 (d, $^1J(\text{P},\text{C}) = 40.0$ Hz, CH_2P), 46.3 (s, $\text{N}(\text{CH}_3)_2$), 58.4 (s, CH_2N), 126.9 (s, *p*-C), 128.1 (d, $^3J(\text{P},\text{C}) = 5.4$ Hz, *m*-C), 132.6 (d, $^2J(\text{P},\text{C}) = 17.7$ Hz, *o*-C) [Assignment of *o*- and *m*-C based on lit.¹⁷], 150.2 ppm (d, $^1J(\text{P},\text{C}) = 20.0$ Hz, *i*-C). ^{31}P NMR (81 MHz, $[\text{D}_8]\text{THF}$): δ 0.4 ppm.

X-ray structure determination of **1b**

X-ray measurement of a suitable single crystal of **1b** was performed on a Stoe IPDS diffractometer with MoK_α radiation ($\lambda = 0.71073$ Å, graphite monochromator). The structure was solved by direct methods (SHELXS-86¹⁸) and refined using full-matrix least-squares procedures on F^2 (SHELXL-93¹⁹). Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms at C1 were found in the difference Fourier map and refined isotropically. The other H atoms were placed in calculated positions according to the „riding model“ with fixed (methyl H atoms) and freely refined displacement parameters, respectively. Crystal data, details of data collection, structure solution and refinement are summarized in Table 1.

Table 1. Crystal data collection and processing parameters for complex **1b**.

Formula	$\text{C}_{40}\text{H}_{60}\text{MgN}_2\text{O}_2\text{F}_2$	Formula weight	687.15
Crystal size, mm	0.20 x 0.20 x 0.10	Temperature, K	220(2)
Crystal system	monoclinic	Space group	$A2/n$
<i>a</i> , Å	20.478(5)	<i>b</i> , Å	8.788(6)
<i>c</i> , Å	23.234(7)	β , °	98.54(3)
<i>V</i> , Å ³	4135(3)	<i>Z</i>	4
D_{calcd} , g cm ⁻³	1.104	$\mu(\text{MoK}_\alpha)$, cm ⁻¹	1.53
<i>F</i> (000)	1488	Scan range, °	$2.01 < \theta < 23.50$
Reflns measured	6659	Reflns unique, R_{int}	2989, 0.1208
Reflns with $I > 2\sigma(I)$	1874	Parameters refined	233
Goodness-of-fit on F^2	0.962	ρ (max/min), e Å ⁻³	0.419/–0.535
<i>R</i> 1, <i>wR</i> 2 [$I > 2\sigma(I)$]	0.0620, 0.1574	<i>R</i> 1, <i>wR</i> 2 (all data)	0.1006, 0.1776
Deposition number ¹⁹	CCDC-159772		

RESULTS AND DISCUSSION

N,N,N',N'-Tetramethylethylenediamine (tmeda) adducts of phosphinomethyl lithium compounds $[\{\text{LiCH}_2\text{PR}_2(\text{tmeda})\}_2]$ (*R* = Me, Ph) react with stoichiometric amounts of magnesium chloride in tetrahydrofuran to give bis(phosphinomethyl)magnesium compounds **1** (Scheme 1). In the case of the *P,P*-dimethylphosphinomethyl derivative, the addition of diethyl ether to the reaction solution leads to an adduct with lithium chloride $\text{Mg}(\text{CH}_2\text{PMe}_2)_2 \cdot 2\text{LiCl}$ **1a**, that does not contain tmeda. In the case of the *P,P*-diphenylphosphinomethyl derivative, the addition of diethyl ether to the reaction solution results in the formation of the tmeda complex $[\text{Mg}(\text{CH}_2\text{PPh}_2)_2(\text{tmeda})]2\text{Et}_2\text{O}$ **1b**. The two Et_2O molecules of crystallization are rapidly lost *in vacuo* yielding $[\text{Mg}(\text{CH}_2\text{PPh}_2)_2(\text{tmeda})]$ **1b'**.

Compounds **1** were isolated as colorless powders (**1a**, **1b'**) or crystals (**1b**) which are very sensitive against air and moisture. The identities of compounds **1** were confirmed by microanalysis and NMR spectroscopy (^1H , ^{13}C , ^{31}P) and by X-ray crystallography (**1b**). The methylene protons of **1b'** are shifted downfield by 0.39 ppm with respect to its lithium analogue (0.02 ppm in **1b'** versus –0.37 ppm in $[\{\text{LiCH}_2\text{PPh}_2(\text{tmeda})\}_2]$ ¹⁷). The ^{13}C resonances of the methylene carbon atoms (AA'X or – taking into account the isotopic shift of ^{13}C – ABX spin systems; A, B = ^{31}P , X = ^{13}C) are split into a doublet. This appearance points to weakly coupled systems ($J_{\text{AA}'} \approx 0$ Hz, $J_{\text{A}'\text{X}} \approx 0$ Hz) that were analyzed as first order spectra ($^1J(\text{P},\text{C}) = 28.0$ Hz **1a**, $^1J(\text{P},\text{C}) = 20.0$ Hz **1b'**).

Scheme 1

Figure 1. Molecular structure and numbering scheme of $[\text{Mg}(\text{CH}_2\text{PPh}_2)_2(\text{tmeda})] \cdot 2\text{Et}_2\text{O}$ **1b**. Ellipsoids are drawn at 30 % probability. Et_2O molecules are omitted.

The molecular structure of complex **1b** along with the atom numbering scheme is shown in Figure 1. Selected bond lengths and angles are listed in Table 2. The structure consists of the monomeric magnesium complex and two diethyl ether molecules without any unusual intermolecular interaction between them (shortest intermolecular distance between non-hydrogen atoms: > 3.5 Å). The magnesium complex exhibits crystallographically imposed C_2 symmetry.

Table 2. Selected bond distances (in Å) and bond angles (in °) for **1b**.

Mg–C1	2.171(4)	P–C5	1.844(4)
Mg–N	2.226(4)	P–C11	1.839(4)
P–C1	1.792(4)		
C1–Mg–C1' ^{a)}	130.0(2)	Mg–C1–P	114.8(2)
N–Mg–N'	82.3(2)	C1–P–C5	108.1(2)
C1–Mg–N	107.8(2)	C1–P–C11	101.1(2)
C1–Mg–N'	109.3(2)	C5–P–C11	99.0(2)

a) Symmetry transformation for equivalent atoms: $x \rightarrow -x + 1/2, y \rightarrow -y + 1/2, z \rightarrow z$.

Magnesium adopts a tetrahedral coordination with remarkable deviations from the ideal geometry. Due to the small “bite” of the tmeda ligand the angle N–Mg–N' amounts to 82.3(2)° as in other magnesium tmeda complexes (median 82.1°; lower/upper quartile 80.7/83.0° for 25 data points²⁰). On the other hand, the angle C–Mg–C is significantly widened up (130.0(2)°). The C–Mg–N angles are close to the ideal tetrahedral angle (107.8(2)°, 109.3(2)°).

The phosphinomethyl ligands are η^1 - (κC -) bound. The Mg–C bond lengths (2.171(4) Å) are in the range of those in complexes $[\text{MgR}_2(\text{tmeda})]$ (R = Me, Et, *sec*-Bu) (2.137(6)–2.181(3) Å)^{21–23} and in $[\text{Mg}(\text{CH}_2\text{SR})_2(\text{thf})_3]$ (R = Me, Ph) (2.168(6)–2.196(3) Å).¹⁴ The bond length between the trivalent phosphorus and the methylene group (1.792(4) Å) is in the range of those in quaternary phosphonium compounds (median 1.802 Å; lower/upper quartile 1.790/1.812 Å²⁷). The P–CH₂ bond is even significantly shorter than the P–C_{Ph} distances (1.839(4) and 1.844(4) Å) in spite of the smaller covalent radii of sp² hybridized carbons in comparison with sp³ hybridized ones. Expected values (median; lower/upper quartile in parentheses) for P–C_{sp3} and P–C_{aryl} in trivalent phosphorus compounds are 1.857 Å (1.840/1.870 Å) and 1.837 Å (1.830/1.844 Å), respectively.²⁴ The same observation was made in phosphinomethyl lithium compounds^{16,17,25} and it seems likely, that this in part arises from a stabilizing influence on the carbanionoid center of phosphorus by polarisation.²⁶ The angles around phosphorus are between 99.0(2) and 108.1(2)°. From the structure of complex **1b** it is evident that phosphorus atoms of the *P,P*-diphenylphosphinomethyl ligands are not coordinated to magnesium. The structure of complex **1a** is unknown yet. Formation of a tmeda-free complex may indicate that the stronger Lewis-basic phosphorus atoms of the Me₂PCH₂ ligands are coordinated to magnesium or lithium.

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