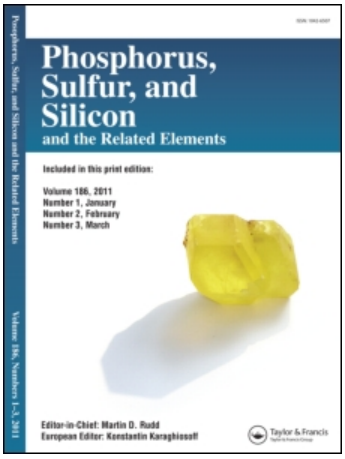

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PREPARATION AND NMR-DATA OF SOME NEW PHOSPHONIUM BROMIDES $[R_2P(NHR')_2]Br$ AND OF IMINOPHOSPHINIC ACID AMIDES $R_2P(NR')(NHR')$

Martin Düppmann[a]; Wilhelm Kuchen[a]; Wilfried Peters[a]
[a] Institut für Anorganische Chemie und Strukturchemie I der Heinrich-Heine-Universität, Düsseldorf, Germany

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PREPARATION AND NMR-DATA OF SOME NEW PHOSPHONIUM BROMIDES $[R_2P(NHR')_2]Br$ AND OF IMINOPHOSPHINIC ACID AMIDES $R_2P(NR')(NHR')$

MARTIN DÜPPMANN, WILHELM KUCHEN* and WILFRIED PETERS

Institut für Anorganische Chemie und Strukturchemie I der Heinrich-Heine-Universität, Universitätsstr. 1, 40225 Düsseldorf, Germany

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The synthesis and the ^{31}P-, ^{1}H-, ^{13}C- and ^{29}Si-NMR spectra of some new Di(organylamino)-diorganylphosphonium bromides $[R_2P(NHR')_2]Br$ **1** (R = ^{i}Pr, Ph; R′ = Me, Et, ^{i}Pr) and of Iminophosphinic acid amides $R_2P(NR')(NHR')$ (R = Et, ^{t}Bu, Ph; R′ = $SiMe_3$) **2** are reported. **1** and **2** can be converted into the Li-salts of ligands $R_2P(NR')_2^-$ that are potential chelate ligands in metal complexes.

Keywords: Phosphonium bromides $[R_2P(NHR')_2]Br$; Iminophosphinic acid amides $R_2P(NR')(NHR')$; ^{31}P-, ^{1}H-, ^{13}C- and ^{29}Si-NMR spectra

INTRODUCTION

Tetracoordinated bischelates $[R_2P(X)NR']_2Ni$ (X = O, S) show a great variety of spectroscopic, magnetic and structural properties that strongly depend on R, R′ and X. Some compounds $[^{t}Bu_2P(O)NR']_2Ni$ are in so far unique as these are the only planar and *paramagnetic* Ni(II)-complexes hitherto known.[1–3] These complexes can be prepared by a metathesis reaction of $R_2P(X)NR'Li$ with nickel halides.

Considering that transition metal chelates of the general type $[R_2P(NR')_2]_nM$ are still unknown we tried to prepare a series of ligands $R_2P(NR')_2^-$ in order to study the effect that substituents R and R′ as well as substitution of X = O,

*Corresponding author.

		a	**b**	**c**	**d**
$[R_2P(NHR')_2]Br$	R:	^iPr	^iPr	Ph	^iPr
1	R':	Me	Et	Et	^iPr
		a	**b**[5]	**c**[6]	
$R_2P(NR')NHR'$	R:	Et	^tBu	Ph	
2	R':	$SiMe_3$	$SiMe_3$	$SiMe_3$	

S by the isovalence electronic group NR' have on the complexing ability and the properties of the corresponding Ni(II)-bischelates.[4]

In our experience[4] ligands $R_2P(NR')_2^-$ are conveniently obtained as Li-salts from phosphonium bromides **1** or iminophosphinic acid amides $R_2P(NR')(NHR')$ **2** by deprotonation with ^{n}BuLi.

For this purpose we prepared compounds **1a–d** and **2a–c**. In case of **2b** and **c** that have been previously reported[5,6] we communicate additional NMR-data.

RESULTS

Phosphonium Bromides 1a–d

Following a method reported by Cristau and Garcia[7] compounds **1a–d** were prepared by adding bromine to diorganylchlorophosphine according to equation (1) followed by the reaction of the resulting phosphorane with the corresponding amine (equation (2)).

The bromides form colorless crystals that are more or less soluble in $CHCl_3$ or CH_2Cl_2 and may be exposed to moist air for some time without noticeable decomposition. Reaction of **1** with 2 moles of ^{n}BuLi affords the Li-salts of iminophosphinic acid amides according to equation (3).[6] These may be in situ subjected to the metathesis reaction with metal halides mentioned above.

$$R_2PCl + Br_2 \rightarrow [R_2PClBr_2] \quad (1)$$

$$[R_2PClBr_2] + 4R'NH_2 \rightarrow \mathbf{1} + 2\ R'NH_3X\ (X = Br, Cl) \quad (2)$$

$$\mathbf{1} + 2\ ^nBuLi \rightarrow R_2P(NR')_2Li + LiBr + 2^nBuH \quad (3)$$

TABLE I δ ^{31}P-data of **1** and **2** ($CDCl_3$) and of the corresponding salts $R_2P(NR')_2Li$ (thf), (δ/ppm); *lit.[10]: $Ph_2P(NSiMe_3)_2Li \cdot 2$ thf, 7.4 (C_6D_6).

	a	*b*	*c*	*d*
1	66.1	63.7	37.2	60.0
$R_2P(NR')_2Li$	55.3	65.8	11.9	44.2
	a	**b**	**c**	
2	23.3	30.5	0.2[9]	
$R_2P(NR')_2Li$	35.5	26.9	7.2*	

Iminophosphinic Acid Amide 2a

In analogy to **2b, c** compound **2a** was prepared according to the procedure of Paciorek and Kratzer[8] from diethylphosphine and trimethylsilyl azide (equation (4)).

$$Et_2PH + 2\ SiMe_3N_3 \rightarrow \mathbf{2a} + 2\ N_2 \qquad (4)$$

2a is a colorless oil that can be destilled under reduced pressure. It is rather stable with respect to moist air and soluble in $CHCl_3$, CH_2Cl_2 or toluene.

Ligands $R_2P(NR')_2^-$

Conversion of **1** and **2** with ^{n}BuLi may be controlled by ^{31}P-NMR. On addition of the required amounts of ^{n}BuLi in hexane to a solution of **1** or **2** in thf the resonance of the starting compound disappears completely and a new singlet is observed that may be assigned to the corresponding salt $R_2P(NR')_2Li$ (Table I). In situ reaction of the Li-salts with suitable metal halides (e.g. Ni(dme)Br_2, $CoBr_2$, $CrCl_3(thf)_3$) afforded chelate complexes of the general type $[R_2P(NR')_2]_nM$[4].

EXPERIMENTAL

Melting points were determined in closed tubes on a melting point apparatus 510 N (Büchi, Switzerland) using a set of calibrated thermometers and are uncorrected.

$^{31}P\{^1H\}$-, $^{13}C\{^1H\}$-, ^1H- and ^{29}Si-NMR spectroscopy: AM 200 (Bruker-Physik, Karlsruhe) using 85% H_3PO_4 as external (^{31}P) and TMS as internal reference (^1H, ^{13}C) and as external reference (^{29}Si). Downfield shifts are positive. Chemical shift values δ (ppm) and coupling constants J (Hz) were obtained by first-

order-analysis. Signal assignments were derived from H,H- and C,H-COSY spectra.

EI-MS spectrometry: MAT 311 A (Varian, Bremen).

1 and **2** were prepared with exclusion of moisture under nitrogen.

Phosphonium bromides 1

General method of preparation: 150 mmoles of Br_2 in 200 mL of CH_2Cl_2 are added with stirring to 150 mmoles of R_2PCl in 100 mL of CH_2Cl_2 at 0°C. Subsequently 600 mmoles of the amine $R'NH_2$ are slowly passed into the reaction mixture that is then stirred for 2 h at room temperature. After filtration the solvent is removed under reduced pressure and the residue crystallized from the solvents or solvent mixtures stated below. The yields are 50%–60%.

Di(methylamino) diisopropylphosphoniumbromide 1a

Crystals from Ether-CH_2Cl_2 (50:50 vol.%) after several days at -30°C; mp: 150°C (decomp.).

$C_8H_{22}BrN_2P$ (257.2)	calcd.:	C 37.37	H 8.62	N 10.89	P 12.04 %
	found:	C 37.59	H 8.88	N 10.88	P 11.78 %

^{1}H-NMR ($CDCl_3$): δ 1.30 (dd, $^3J_{HH}$ 7.2, $^3J_{PH}$ 17.2, $(CH_3)_2CHP$); 2.28 (dd, $^3J_{HH}$ 5.1, $^3J_{PH}$ 16.2, CH_3NHP); 2.66 (m, *partially hidden*, $(CH_3)_2CHP$); 5.47 (dq, $^3J_{HH}$ 11.6, $^2J_{PH}$ 16.8, CH_3NHP).

$^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 16.9 (d, $^2J_{CP}$ 2.6, CCP); 25.2 (d, $^1J_{CP}$ 74.0, CP); 27.6 (d, $^2J_{CP}$ 3.8 Hz, CNP).

EI-MS (70 eV): m/z 177 ($M\text{-}Br^+$, 17 %).

Di(ethylamino) diisopropylphosphoniumbromide 1b

Crystals from MeCOOEt-CH_2Cl_2 (95:5 vol.%); mp: 115°C (decomp.).

$C_{10}H_{26}BrN_2P$ (285.2)	calcd.:	C 42.11	H 9.19	N 9.82	P 10.86 %
	found:	C 42.39	H 9.30	N 10.10	P 10.76 %

^{1}H-NMR ($CDCl_3$): δ 1.28 (*partially hidden*, CH_3CH_2); 1.30 (dd, $^3J_{HH}$ 7.2, $^3J_{PH}$ 15.7, $(CH_3)_2CHP$); 2.66 (m, $(CH_3)_2CHP$); 3.07 (m, CH_3CH_2NHP); 5.50 (dtr, $^3J_{HH}$ 8.2, $^2J_{PH}$ 16.5, CH_2NHP).

$^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 16.8 (d, $^2J_{CP}$ 2.8, CCP); 18.8 (d, $^3J_{CP}$ 5.7, CCNP); 25.0 (d, $^1J_{CP}$ 73.7, CP); 36.7 (d, $^2J_{CP}$ 3.9, CNP).

EI-MS (70 eV): m/z 205 ($M\text{-}Br^+$, 25 %).

Di(ethylamino)diphenylphosphoniumbromide 1c

Crystals from methanol; mp: 163–165°C (decomp.).

$C_{16}H_{22}BrN_2P$ (353.3)	calcd.:	C 54.40	H 6.28	N 7.93	P 8.77 %
	found:	C 54.22	H 6.36	N 7.89	P 8.29 %

^{1}H-NMR ($CDCl_3$): δ 1.22 (tr, $^3J_{HH}$ 7.1, CH_3CH_2); 3.05 (m, CH_3CH_2NHP); 6.59 (dtr, $^3J_{HH}$ 7.4, $^2J_{PH}$ 14.8, CH_2NHP); 7.54, 8.05 (m, C_6H_5).

^{13}C{^{1}H}-NMR ($CDCl_3$): δ 17.4 (d, $^3J_{CP}$ 5.9, CCNP); 36.5 (d, $^2J_{CP}$ 1.8, CNP); 125.4 (d, $^1J_{CP}$ 125.9, i-C); 130.0 (d, $^3J_{CP}$ 11.4, m-C); 133.1 (d, $^2J_{CP}$ 13.8, o-C); 134.4 (d, $^4J_{CP}$ 2.9, p-C).

EI-MS (70 eV): m/z 273 ($M\text{-}Br^+$, 24 %).

Di(isopropylamino)diisopropylphosphoniumbromide 1d

Crystals from MeCOOEt-CH_2Cl_2 (80:20 vol. %); mp: 199°C (decomp.).

$C_{12}H_{30}BrN_2P$ (313.3)	calcd.:	C 46.01	H 9.65	N 8.94	P 9.89 %
	found:	C 45.86	H 9.85	N 8.76	P 9.60 %

^{1}H-NMR ($CDCl_3$): δ 1.18 (d, $^3J_{HH}$ 7.1, $(CH_3)_2CHN$); 1.29 (dd, $^3J_{HH}$ 7.1, $^3J_{PH}$ 15.8, $(CH_3)_2CHP$); 2.59 (m, $(CH_3)_2CHP$); 3.38 (m, $(CH_3)_2CHNH$); 5.28 (dd, $^3J_{HH}$ 10.1, $^2J_{PH}$ 17.2, CHNHP).

^{13}C{^{1}H}-NMR ($CDCl_3$): δ 16.3 (d, $^2J_{CP}$ 2.6, CCP); 24.4 (d, $^1J_{CP}$ 74.3, CP); 26.0 (d, $^3J_{CP}$ 3.8, CCNP); 44.1 (d, $^2J_{CP}$ 4.1).

EI-MS (70 eV): m/z 233 ($M\text{-}Br^+$, 25 %).

(Trimethylsilylimino)diethylphosphinic acid trimethylsilylamide 2a

After adding 140 mmoles of Me_3SiN_3 to 50 mmoles of Ph_2PH[11] at 0°C the reaction mixture is slowly warmed to 85°C and kept at this temperature for 16 h. Subsequently unreacted trimethylsilyl azide is distilled off at 40 °C under reduced pressure and the oily residue fractionated, yield 75%; bp: 55°C (0.02 mbar).

$C_{10}H_{29}N_2PSi_2$ (264.5)	calcd.:	C 45.41	H 11.05	N 10.59	P 11.71 %
	found:	C 45.67	H 11.43	N 10.59	P 11.48 %

^{1}H-NMR ($CDCl_3$): δ 0.11 (s, $(CH_3)_3Si$); 1.10 (m, CH_3CH_2P); 1.53 (m, CH_3CH_2P).

^{13}C{^{1}H}-NMR (C_6D_6): δ 2.9, 5.3 (s, CSi); 7.2 (d, $^2J_{CP}$ 4.8, CCP); 27.4 (d, $^1J_{CP}$ 78.2, CP).

^{29}Si-NMR (C_6D_6): δ -16.0 ($NHSiMe_3$); 4.7 ($NSiMe_3$).

EI-MS (70 eV): m/z 264 (M^+, 8%).

(Trimethylsilylimino)ditert.butylphosphinic acid trimethylsilylamide 2b[5]

$^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 3.0, 5.2 (d, $^3J_{CP}$ 1.6, CSiNP); 28.3 (d, $^2J_{CP}$ 1.6, CCP); 37.8 (d, $^1J_{CP}$ 74.3, CP).

^{29}Si-NMR (C_6D_6): δ -19.8 ($NHSiMe_3$), 4.5 ($NSiMe_3$).

(Trimethylsilylimino)diphenylphosphinic acid trimethylsilylamide 2c[6]

$^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 2.2, 4.4 (s, CSi); 128.4 (d, $^3J_{CP}$ 12.6, m-C); 130.7 (d, $^4J_{CP}$ 2.9, p-C); 131.5 (d, $^2J_{CP}$ 10.7, o-C), 139.0 (d, $^1J_{CP}$ 119.0, i-C).

^{29}Si-NMR (C_6D_6): δ -14.6 ($NHSiMe_3$); 6.2 ($NSiMe_3$).

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