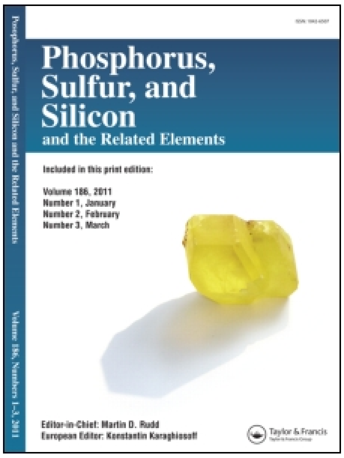

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SOME NEW PHOSPHINIC AMIDES $R_2P(O)NHR'$

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SOME NEW PHOSPHINIC AMIDES $R_2P(O)NHR'$

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P,P-Diorganylphosphinic amides $R_2P(O)NHR'$ (R = ^{t}Bu, ^{i}Pr, Ph; R′ = Et, Pr, Cy, ^{i}Pr, ^{t}Bu, Ph, etc.) have been prepared by reaction of R_2PCl with the corresponding lithiated amine followed by oxidation with H_2O_2. Their ^{31}P and ^{13}C NMR spectra are discussed.

Key words: P,P-Diorganylphosphinic amides, phosphorus-31 NMR, carbon-13 NMR.

INTRODUCTION

Phosphinic amidato ligands $[R_2P(O)NR']^-$ are in so far unique as some of them form Ni(II) complexes $Ni[R_2P(O)NR']_2$ (R = ^{t}Bu; R′ = ^{i}Pr, Cy, ^{t}Bu) that are planar and *paramagnetic*.[1,2] These are obtained in a methathesis reaction between the lithiated amides $R_2P(O)NR'Li$ and $NiCl_2(PPh_3)_2$. As there is evidence that the complexing ability of the ligands as well as coordination geometry and magnetic properties of the resulting complexes strongly depend on the nature of R and R′ we decided to investigate their influence more systematically. For this purpose we synthesized the phosphinic amides **1–3** that are described below.

RESULTS AND DISCUSSION

Preparation of Phosphinic Amides **1–3**

Several methods for the preparation of phosphinic amides have been reported in the literature.[3,4] To our experience in case of **1–3** best yields (60–70%) are obtained by the following procedure[5,6]:

$$R'NH_2 \xrightarrow[-\,C_4H_{10}]{n\text{-BuLi}} R'NHLi \xrightarrow[-\,LiCl]{R_2PCl} R_2P\text{-}NHR'$$

$$R_2P\text{-}NHR' \xrightarrow[-\,H_2O]{+\,H_2O_2} \mathbf{1-3}$$

When crystallized from acetone **1–3** form colourless needles that are easily soluble in $CHCl_3$ or THF. They may be exposed to moist air for a longer period of time without noticeable decomposition. Some properties of **1–3** are listed in Table I.

TABLE I

Some physical data of **1–3** ($\delta^{31}P$: $CDCl_3$,* C_6D_6,† acetone-d_6)

$R_2P(O)NHR'$	*R'*		M.P. [°C]	$\delta^{31}P$ [ppm]
R = ^tBu	*Et*	**1a**	193	55.42
	Pr	**1b**	182	55.46
	(±) ^sBu	**1c**	176	55.24
	(-)Mb	**1d**	165	54.26 *
	1-Ad	**1e**	220	56.45
	^tPen	**1f**	141	56.40
	Ph	**1g**	176	55.84 †
R = ^iPr	^iPr	**2a**	201	49.42 *
	Cy	**2b**	157	50.91 *
	^tBu	**2c**	191	52.07
	Ph	**2d**	135	52.53 †
R = Ph	^iPr	**3a**	148	19.71 *
	Cy	**3b**	194	19.86 *
	^tBu	**3c**	124	18.19 *

^sBu = *sec*-Butyl; Mb = α-Methylbenzyl; 1-Ad = 1-Adamantyl; ^tPen = *tert*-Pentyl.

TABLE II

$^{13}C\{^1H\}$ NMR data of $^tBu_2P(O)NHR'$ **1a–g** ($CDCl_3$,^{a} C_6D_6,^{b} acetone-d_6).
δ/ppm, (J/Hz)

	R'	δ_{PC} ($^1J_{PC}$)	δ_{PCC}	δ_{PNC} ($^2J_{PC}$)	δ_{PNCC} ($^3J_{PC}$)	δ_{PNCCC}	δ_{PNCCCC}	$\delta_{PNCCCCC}$
1a	*Et*	37.04 (77.0)	27.40	36.36 (2.7)	19.20 (4.4)			
1b	*Pr*	37.16 (76.7)	27.44	43.44 (2.9)	26.88 (4.1)	11.93		
1c	*(±)* ^sBu	37.03 (77.9)	27.46	48.49 (3.0)	23.66 (3.1)	10.75		
		36.90 (76.7)	27.44		33.34 * (3.9)			
1d	*(-)Mb* ^{a}	37.36 (77.9)	27.59	50.83	148.07 (3.3)	127.20	129.32	127.51
		36.65 (75.5)	27.50		n.o.*†			
1e	^tPen	37.36 (76.4)	27.82	55.58 (4.8)	30.01 (1.4)	9.58		
					39.50 * (5.4)			
1f	*1-Ad*	37.11 (76.0)	27.85	53.44 (4.6)	46.91 (2.7)	30.86	36.92	
1g	*Ph* ^{b}	38.29 (75.8)	27.34	146.20 (3.3)	120.21 (3.8)	129.63	121.36	

* δ_{PNCCH_3}, † covered by δ_{PCCH_3}; n.o.: not observed.

NMR Spectroscopic Results

The $\delta^{31}P$ values of **1–3** cover a range from 18–57 ppm. As shown in Table I the influence of R′ on the chemical shift is minor while a change of R clearly effects

TABLE III

^{13}C{^{1}H} NMR data of ^{i}Pr$_2$P(O)NHR′ 2a–d (C$_6$D$_6$,^{a} acetone-d$_6$). δ/ppm, (J/Hz)

	R′	δ_{PC} ($^1J_{PC}$)	δ_{PCC} ($^2J_{PC}$)	δ_{PNC} ($^2J_{PC}$)	δ_{PNCC} ($^3J_{PC}$)	δ_{PNCCC}	δ_{PNCCCC}
2a	^{i}Pr	27.10 (83.0)	16.85 (3.1) 16.44 (3.1)	42.80 (1.8)	27.21 (3.7)		
2b	Cy	26.98 (83.0)	16.77 (3.1) 16.38 (3.1)	49.74 (2.1)	38.10 (3.3)	26.38	26.62
2c	^{t}Bu ^{a}	28.04 (82.9)	17.00 (2.9) 16.50 (2.9)	51.99 (4.0)	33.35 (3.2)		
2d	Ph ^{a}	27.54 (82.8)	16.73 (3.1) 16.50 (3.1)	145.90 (3.3)	119.79 (5.2)	129.77	121.30

TABLE IV

^{13}C{^{1}H} NMR data of Ph$_2$P(O)NHR′ 3a–c (C$_6$D$_6$). δ/ppm, (J/Hz)

	R′	δ_{PC} ($^1J_{PC}$)	δ_{PCC} ($^2J_{PC}$)	δ_{PCCC} ($^3J_{PC}$)	δ_{PCCCC} ($^4J_{PC}$)	δ_{PNC} ($^2J_{PC}$)	δ_{PNCC} ($^3J_{PC}$)	δ_{PNCCC}	δ_{PNCCCC}
3a	^{i}Pr	135.79 (127.4)	133.35 (9.2)	129.16 (12.1)	132.02 (2.8)	44.52 (1.4)	26.60 (5.7)		
3b	Cy	135.93 (127.8)	133.18 (9.1)	129.17 (12.2)	132.10 (2.7)	51.44 (3.5)	37.21 (3.7)	26.15	26.37
3c	^{t}Bu	137.59 (126.6)	132.81 (9.4)	129.05 (12.3)	131.80 (2.7)	53.51 (2.8)	32.71 (4.5)		

different shielding of the phosphorus nucleus. In agreement with earlier results[5,7,8] enlargement of the RPR angle is accompanied by a significant downfield shift.

The ^{13}C{^{1}H} NMR spectra (Tables II–IV) are almost identical with those of the analogous phosphinothioic amides R$_2$P(S)NHR′ (R = ^{i}Pr, ^{t}Bu; R′ = Et, ^{i}Pr, Cy, ^{t}Bu, 1-Ad).[5] Again it is found that R′ has only little influence on the chemical shifts of the carbons in R. As replacement of one of the protons at the α-C atom in R′ by another carbon is generally accompanied by deshielding δ_{PNC} is shifted downfield in the sequence Et > ^{s}Bu > ^{t}Pen, and so is δ_{PNCC}.

While the chemical shifts of the phosphinic amides are practically identical with those of their thio analogues the $^1J_{PC}$ values are much larger in the former case.

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{^{1}H}, ^{13}C{^{1}H} and ^{1}H NMR spectroscopy: AM 200 (Bruker-Physik, Karlsruhe) using 85% H$_3$PO$_4$ as external (^{31}P) and TMS as internal reference (^{1}H, ^{13}C). Downfield shifts are positive.

TABLE V

Analytical and ^{1}H NMR data of ^{t}Bu$_2$P(O)NHR′ **1a–g** (CDCl$_3$,^{d} C$_6$D$_6$,^{c} acetone-D$_6$). Molecular weight, δ/ppm, (*J*/Hz)

	formula (MW)	δ_{PCCH} ($^3J_{PH}$)	δ_{PNH} ($^2J_{PH}$)	δ_{NCH} ($^3J_{HH}$)	δ_{PNCCH} ($^3J_{HH}$)	δ_{PNCCCH} ($^3J_{HH}$)		analytical data		
								C	H	N
1a	$C_{10}H_{24}NOP$ (205.2)	1.24 (13.6)	1.82	3.13 (7.1)	1.17 (6.7)		calcd. found	58.51 58.39	11.78 11.83	6.82 6.68
1b	$C_{11}H_{26}NOP$ (219.3)	1.24 (13.6)	1.89	3.03 (6.9)	1.54 (mc)	0.93 (7.4)	calcd. found	60.24 60.05	11.95 11.99	6.39 6.28
1c[*]	$C_{12}H_{28}NOP$ (233.3)	1.24 (13.7)	2.64	3.38 (mc)	1.18 (6.5)	0.92 (7.4)	calcd. found	61.77 61.55	12.10 12.15	6.00 5.93
1d[a,d]	$C_{16}H_{28}NOP$ (281.4)	1.42 (13.5) 1.24 (13.5)	2.65 (11)	5.10 (mc)	1.67 (6.8)		calcd. found	68.30 68.41	10.03 10.10	4.98 4.93
1e[c]	$C_{13}H_{30}NOP$ (247.4)	1.24 (13.6)	n.o.	-	1.96 (mc)	2.07 (mc)	calcd. found	63.12 62.99	12.22 12.43	5.66 5.53
1f[†]	$C_{18}H_{34}NOP$ (311.5)	1.23 (13.6)	n.o.	-	1.34 1.57 (7.3)	0.92 (7.3)	calcd. found	69.42 69.41	11.00 11.04	4.50 4.31
1g[b,e]	$C_{14}H_{24}NOP$ (253.3)	1.43 (13.8)	5.95 (13)	-			calcd. found	66.38 66.43	9.55 9.39	5.53 5.44

δ_{PNCCH_2}: [*] 1.65, 1.42 (mc); [†] 1.57 (6.8). $\delta_{C_6H_5}$: [a] 7.24 - 7.58; [b] 6.85 - 7.65. [c] $\delta_{PNCCCCH}$: 1.64 (mc); n.o.: not observed; mc: multiplet centred.

TABLE VI

Analytical and ^{1}H NMR data of ^{i}Pr$_2$P(O)NHR′ **2a–d** (C$_6$D$_6$,† acetone-d$_6$). Molecular weight, δ/ppm, (*J*/Hz)

	formula (MW)	δ_{PCH} ($^2J_{PH}$)	δ_{PCCH} ($^3J_{PH}/^3J_{HH}$)	δ_{PNH} ($^2J_{PH}$)	δ_{PNCH} ($^3J_{PH}$)	δ_{PNCCH} ($^3J_{HH}$)		analytical data		
								C	H	N
2a	$C_9H_{22}NOP$ (191.3)	1.88 (mc)	1.23 (15.2 / 7.1) 1.35 (15.2 / 7.1)	2.35 (11)	3.87 (mc)	1.34 (6.3)	calcd. found	56.52 56.68	11.59 11.79	7.32 7.10
2b	$C_{12}H_{26}NOP$ (231.3)	1.80 (mc)	1.32 (15.2 / 7.1) 1.17 (15.2 / 7.1)	2.50 (11)	3.45 (mc)	[a]	calcd. found	62.31 62.01	11.33 11.35	6.06 6.04
2c[†]	$C_{10}H_{24}NOP$ (205.3)	2.05 (mc)	1.25 (15.2 / 7.0)	3.19	-	1.47	calcd. found	58.51 58.37	11.78 12.07	6.82 6.56
2d[†]	$C_{12}H_{20}NOP$ (225.3)	2.40 (mc)	1.36 (15.7 / 7.2) 1.31 (15.2 / 7.2)	n.o.	-	7.54 [b] (mc)	calcd. found	63.98 63.93	8.95 8.99	6.22 6.16

[a] δ_{PNCCH} - $\delta_{PNCCCCH}$: 1.10 - 2.30; [b] δ_{PNCCCH}: 7.24 (mc), $\delta_{PNCCCCH}$: 6.94 (mc); n.o.: not observed; mc: multiplet centred.

General method for preparation of compounds **1–3**: An equimolar quantity of *n*-butyllithium dissolved in hexane was added to a solution of the amine in THF. After refluxing for 1 h an equimolar quantity of the corresponding chlorodiorganylphosphine in THF was added and the reaction mixture refluxed for another 6 h. Then the solvents were removed and the resulting residue dissolved in toluene. Oxidation

TABLE VII

Analytical and ^1H NMR data of $Ph_2P(O)NHR'$ **3a–c** (C_6D_6). Molecular weight, δ/ppm, (J/Hz)

	formula	$\delta_{PC_6H_5}$	δ_{PNH}	δ_{PNCH}	δ_{PNCCH}		analytical data		
	(MW)		($^2J_{PH}$)	($^3J_{PH}$)	($^3J_{HH}$)		C	H	N
3a	$C_{15}H_{18}NOP$	7.35 - 8.40	2.88	3.47	1.26	calcd.	69.48	6.99	5.40
	(259.3)		(10.4)	(mc)	(6.4)	found	69.57	6.75	5.48
3b	$C_{18}H_{22}NOP$	7.35 - 8.30	3.90	3.15	[a]	calcd.	72.22	7.41	4.68
	(299.4)		(mc)	(mc)		found	72.16	7.31	4.56
3c	$C_{16}H_{20}NOP$	7.30 - 8.30	n.o.	-	1.46	calcd.	70.31	7.38	5.12
	(273.3)					found	70.15	7.30	5.05

[a] δ_{PNCCH} - $\delta_{PNCCCCH}$: 1.10 - 2.40; n.o.: not observed, mc: multiplet centred.

was achieved by cautiously adding the equimolar quantity of H_2O_2 (30% in water) while vigorous stirring. After separating the toluene layer the solvent was evaporated and the residue crystallized from acetone affording colourless needles. Yields 60–70%.

The ^1H NMR and analytical data are given in Tables V–VII.

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