3254 *Inorg. Chem.* **1996,** *35,* 3254−3261

Imide Transfer Properties and Reactions of the Magnesium Imide $((THF)MgNPh)_6$: A Versatile Synthetic Reagent

Warren J. Grigsby, Tony Hascall, Jeffrey J. Ellison, Marilyn M. Olmstead, and Philip P. Power*

Department of Chemistry, University of California, Davis, California 95616

Received November 22, 1995[⊗]

Imide transfer properties of $((THF)MgNPh)_6$ (**1**) and the synthesis of the related species $\{(THF)MgN(1\text{-naphthyl})\}_6 \cdot 2.25THF$ (**2**), via the reaction of dibutylmagnesium with $H_2N(1\text{-naphthyl})$, in a THF/heptane mixture are described. Treatment of **1** with Ph_2CO, $4\text{-}Me_2NC_6H_4NO$, $t\text{-}BuNBr_2$ (**3**), PCl_3, or $MesPCl_2$ (Mes = 2,4,6-$Me_3C_6H_2$-) leads to the isolation of Ph_2CNPh (**4**), $4\text{-}Me_2NC_6H_4NNPh$ (**5**), $t\text{-}BuNNPh$ (**6**), $(PhNPCl)_2$ (**7**), or $(MesPNPh)_2$ (**8**) in moderate yield. Reaction between **1** and $GeCl_2 \cdot dioxane$, $SnCl_2$, or $PbCl_2$ affords the M_4N_4 (M = Ge, Sn, Pb) cubane imide derivative $(GeNPh)_4$ (**9**), $[(SnNPh)_4 \cdot \{MgCl_2(THF)_4\}]_\infty$ (**10**), $(SnNPh)_4 \cdot 0.5PhMe$ (**11**), or $(PbNPh)_4 \cdot 0.5PhMe$ (**12**). Interaction of **1** with Ph_3PO, $(Me_2N)_3PO$, or Ph_2SO furnishes the complex $(Ph_3POMgNPh)_6$ (**13**), $\{(Me_2N)_3POMgNPh\}_6 \cdot 2PhMe$ (**14**), or $(Ph_2SOMgNPh)_6$ (**15**). The addition of 3 equiv of $MgBr_2$ to **1** gives 1.5 equiv of $((THF)Mg)_6(NPh)_4Br_4$ (**16**) in quantitative yield, whereas treatment of **16** with 4 equiv of 1,4-dioxane is an alternative synthetic route to **1**. Compounds **2**, **3**, **9**, **10**, and **14** were characterized by X-ray crystallography. The reactions demonstrate that **1** is a versatile and useful reagent for the synthesis of a variety of main group imides. Crystal data at 130 K with Mo Kα (λ = 0.710 73 Å) radiation for **3** or Cu Kα (λ = 1.541 78 Å) radiation for **2**, **9**, **10**, and **14**: **2**, $C_{93}H_{108}Mg_6N_6O_{7.25}$, a = 28.101(7) Å, b = 35.851(7) Å, c = 36.816(7) Å, Z = 2, space group $Fddd$, R = 0.068 for 3500 ($I > 2\sigma(I)$) data; **3**, $C_4H_9Br_2N$, a = 6.682(2) Å, b = 10.834(3) Å, c = 11.080(3) Å, α = 66.25(2)°, β = 89.88(2)°, γ = 82.53(2)°, Z = 4, space group $P\bar{1}$, R = 0.038 for 2043 ($I > 2\sigma(I)$) data; **9**, $C_{24}H_{20}Ge_4N_4$, a = 10.749(2) Å, b = 12.358(3) Å, c = 35.818(7) Å, Z = 8, space group $Pbca$, R = 0.040 for 2981 ($I > 2\sigma(I)$) data; **10**, $C_{40}H_{52}Cl_2MgN_4O_4Sn_4$, a = 12.770(3) Å, b = 13.554(3) Å, c = 25.839(5) Å, Z = 4, space group $P2_12_12_1$, R = 0.040 for ($I > 2\sigma(I)$) data; **14**, $C_{86}H_{154}Mg_6N_4O_6P_6$, a = 22.478(4) Å, b = 16.339(3) Å, c = 29.387(6) Å, Z = 4, space group $Pbcn$, R = 0.081 for 4696 ($I > 2\sigma(I)$) data.

Introduction

Magnesium imides have their origin in reactions between Grignard reagents and primary arylamines which were originally described by Meunier in 1903, eq 1.[1]

$$PhNH_2 + 2RMgX \xrightarrow[\text{R = alkyl group}]{\text{X = halide}} \text{“}PhN(MgX)_2\text{”} + 2RH \qquad (1)$$

Since that time, magnesium imides have only received intermittent attention,[2] and it was not until 1994 that the structure of an “$RN(MgX)_2$” species was shown to have an adamantyl framework of formula $(Et_2OMg)_6(NR)_4Br_4$ (R = Ph)[3] which presumably arises from the disproportionation shown in eq 2.

$$4\text{“}PhN(MgBr)\text{”}_2 \xrightarrow{\text{L = }Et_2O\text{ or THF}} (LMg)_6(NPh)_4Br_4 + 2MgBr_2 \qquad (2)$$
$$\text{L = THF } (\mathbf{16})$$

Parallel work showed that the reaction between aniline and $MgEt_2$ affords the new halide-free imide species $((THF)MgNPh)_6$ (**1**),[4] featuring a hexagonal prismatic Mg_6N_6 cage structure as shown in eq 3.

$$6Et_2Mg + 6H_2NPh \xrightarrow{\text{THF}} \underset{\mathbf{1}}{((THF)MgNPh)_6} + 12EtH \qquad (3)$$

In addition to the characterization of the imide species themselves, there have been some investigations of the reactions of $ArN(MgBr)_2$ compounds (Ar = variously substituted aromatic rings) with a variety of reagents such as ketones, bifunctional nitroarenes, oxidizing agents, nitrobenzothiazoles, and nitrobenzenes.[5] These reactions were carried out with an “$ArN(MgBr)_2$” species that was not isolated but generated in situ. In contrast, with the exception of some reactions involving cyclopentadienyl halides of titanium or zirconium,[6] there is no information available on the chemistry of the simpler $((THF)MgNPh)_6$ species **1**. In this paper the reactions of this interesting compound with a variety of substrates are reported. In addition an alternative method for the synthesis of **1** by the reaction of readily available **16**, i.e. $((THF)Mg)_6(NPh)_4Br_4$, with 4 equiv of 1,4-dioxane is described.

Experimental Section

General Procedures. All reactions were performed by using modified Schlenk techniques under an inert atmosphere of N_2 or in a Vacuum Atmospheres HE43-2 drybox. Solvents were freshly distilled

---

[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1996.

(1) Meunier, L. *C. R. Hebd. Seances Acad. Sci.* **1903**, *136*, 758.

(2) Petyunin, P. A. *Russ. Chem. Rev.* (*Engl. Transl.*) **1962**, *31*, 100.

(3) Hascall, T.; Olmstead, M. M.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1000.

(4) Hascall, T.; Ruhlandt-Senge, K.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 356.

(5) For example: (a) Okubo, M.; Hayashi, S.; Matsunaga, M.; Uematsu, Y. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2337. (b) Okubo, M.; Aratani, H.; Gondo, T.; Koga, K. *Ibid.* **1983**, *56*, 788. (c) Okubo, M.; Yoshida, S.; Egami, Y.; Matsuo, K.; Nagase, S. *Ibid.* **1987**, *60*, 1741. (d) Okubo, M.; Asao, K.; Hyakutake, H. *Ibid.* **1987**, *60*, 3781. (e) Okubo, M.; Inatomi, Y.; Taniguchi, N.; Imamura, K. *Ibid.* **1988**, *61*, 3881.

(6) Grigsby, W. J.; Olmstead, M. M.; Power, P. P. *J. Organomet. Chem.*, in press.

S0020-1669(95)01510-2 CCC: $12.00

under N_2 from Na/K or Na/K/benzophenone ketyl and degassed twice before use. NMR spectra were obtained on a General Electric QE-300 NMR spectrometer and referenced to an internal standard. ^{31}P NMR spectra were referenced to an external standard, 85% H_3PO_4. IR spectra were obtained by using a Perkin-Elmer 1430 spectrometer. $SnCl_2$, $PbCl_2$, Ph_2CO, Ph_2SO, 4-$(Me_2N)C_6H_4$4NO, Ph_3PO, and Bu_2Mg (1:1 mixture of *n*- and *sec*-Bu 1.0 M in heptane) were purchased commercially and used as received. Aniline and $(Me_2N)_3PO$ were distilled from calcium hydride before use. The compound ((THF)-$MgNPh)_6$ (**1**), which was used in the reactions described below, was synthesized by the reaction of Bu_2Mg and aniline in THF/heptane solution.[6] PCl_3 was distilled prior to use. *t*-$BuNBr_2$ (**3**)[7], $MesPCl_2$,[8] and $GeCl_2$·dioxane[9] were synthesized by literature procedures. 1-Naphthylamine was used as received.

{(THF)MgN(1-naphthyl)}$_6$·2.25THF (2). 1-Naphthylamine (0.72 g, 5 mmol) dissolved in THF (30 mL) was treated with $MgBu_2$ (5 mmol in heptane solution, 5.0 mL). The solution was refluxed for 15 h and filtered through a pad of Celite. The solution was then concentrated to ca. 20 mL and cooled in a −20 °C freezer for 2 days to give yellow crystals of {(THF)MgN(1-naphthyl)}$_6$·2.25THF (**2**) (0.82 g, 0.5 mmol, 62% based on Mg): ^1H NMR (300 MHz, C_7D_8) δ 9.37 (s, br, 1H, H8), 7.70 (d, $J = 7.8$ Hz, 1H, H3), 7.23 (m, 3H, H5−H7), 6.98 (m, 2H, H2, H4), 3.54 (s, 4H, OCH_2), 1.45 (s, 4H, CH_2); ^{13}C NMR (300 MHz, C_7D_8) δ 165.2 (s, C1), 133.3 (s, C5), 129.2 (d), 122.3 (d), 116 (d, C4), 110.3 (d, C2); IR (Nujol) ν 1605 (w), 1565 (m), 1550 (s), 1500 (s), 1280 (s, br), 1220 (m), 1160 (m), 1130 (w), 1080 (ms), 1050 (m), 1020 (ms), 890 (m), 790 (m, sh), 770 (s), 720 (ms), 660 (m), 610 (m), 570 (m), 515 (ms), 425 (m), 390 (m) cm^{-1}. Desolvation problems involving THF did not permit an accurate elemental analysis of this compound.

$Ph_2C{=}NPh$ (4). Benzophenone (0.58 g, 3.2 mmol) was dissolved in diethyl ether (40 mL). ((THF)$MgNPh)_6$(0.60 g, 0.53 mmol) was added via a solids-addition funnel, and the solution was stirred for 16 h. The pale yellow solution was filtered through Celite and then concentrated to incipient crystallization. Cooling the solution in a −20 °C freezer yielded colorless crystals of triphenylimine (**4**) (0.60 g, 2.3 mmol, 73%): mp 112−113 °C (lit. 109 °C);[10] ^1H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, $J = 7.2$ Hz, 2H, *o*-H), 7.52 (m, 3H), 7.34 (m, 4H), 7.23 (m, 3H), 7.01 (t, $J = 7.2$ Hz, 1H, *p*-H), 6.82 (d, $J = 7.2$ Hz, 2H, *o*-H).

4-$Me_2NC_6H_4N{=}NPh$ (5). *N*,*N*-Dimethyl-4-nitrosoaniline (0.60 g, 4.0 mmol) dissolved in diethyl ether (25 mL) was added to a solution of ((THF)$MgNPh)_6$ (0.75 g, 0.67 mmol) dissolved in diethyl ether (25 mL). The green solution rapidly became orange. After 2 h of stirring, the solution was filtered through Celite and concentrated to incipient crystallization. Cooling in a −20 °C freezer over several days yielded yellow crystals of *N*,*N*-dimethyl-4-phenylazoaniline (**5**) (0.60 g, 2.7 mmol, 67%): mp 115 °C (lit. 115 °C);[11] ^1H NMR (300 MHz, C_6D_6) δ 8.21 (d, $J = 9.0$ Hz, 2H, *o*-H), 8.15 (d, $J = 7.5$ Hz, 2H, *o*-H), 7.24 (d, $J = 7.2$ Hz, 2H, *m*-H), 7.09 (t, $J = 7.5$ Hz, 1H, *p*-H), 6.44 (d, $J = 9.0$ Hz, 2H, *m*-H).

***t*-BuN=NPh (6).** ((THF)$MgNPh)_6$ (0.86 g, 0.76 mmol) was dissolved in diethyl ether (40 mL). Dioxane (1 mL, 11.7 mmol) was added and the solution cooled with a dry ice/acetone bath. *t*-$BuNBr_2$ (**3**) (1.06 g, 4.59 mmol) dissolved in diethyl ether (20 mL) was added dropwise, and the solution was allowed to warm to room temperature and stirred for a further 12 h. The dark brown solution was filtered through Celite, and the solvent was removed under reduced pressure. Distillation of the remaining dark brown residue afforded an orange oil identified as 1-*tert*-butyl-2-phenyldiazene (**6**) (0.20 g, 1.23 mmol, 27%): bp (70−74 °C/2.0 mmHg; lit. 32−35 °C/0.05 Torr);[12] ^1H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, $J = 8.1$ Hz, 2H, *o*-H), 7.50 (m, 3H, *m*-H, *p*-H), 1.31 (s, 9H, *t*-Bu).

***cis*-$(PhNPCl)_2$ (7).** ((THF)$MgNPh)_6$ (0.93 g, 0.83 mmol) was dissolved in THF (30 mL). Dioxane (1 mL, 11.7 mmol) and freshly distilled PCl_3 (0.29 mL, 3.32 mmol) were added via syringe. The solution immediately turned yellow with warming. After 18 h of stirring, all volatile material was removed under reduced pressure, and the resulting white solid was extracted with warm toluene (40 mL). The solution was filtered through a frit and concentrated to *ca*. 5 mL. Slow cooling yielded fine white crystals of *cis*-$(PhNPCl)_2$ (**7**) (0.23 g, 0.73 mmol, 27% based on phosphorus): mp = 110−112 °C (lit. 153−154 °C);[13] ^1H NMR (300 MHz, C_6D_6) δ 6.97 (t, $J = 8.1$ Hz, 2H, *m*-H), 6.83 (m, 3H, *o*, *p*-H); ^{13}C NMR (300 MHz, C_6D_6) δ 138.1 (s, $J_{P-C} = 10.0$ Hz, ipso-C), 130.1 (d, *m*-C), 123.9 (d, *p*-C), 117.1 (d, $J_{P-C} = 6.9$ Hz, *o*-C); ^{31}P NMR (300 MHz, C_6D_6) δ 199.8 (s); IR (Nujol) ν 1590 (s), 1485 (s), 1264 (vs), 1095 (w), 1072 (w), 1030 (w), 915 (vs), 745 (ms), 680 (m), 470 (m), 390 (mw) cm^{-1}.

$(MesPNPh)_2$ (8). ((THF)$MgNPh)_6$ (0.75 g, 0.67 mmol) was dissolved in THF. Dioxane (1 mL, 11.7 mmol) and $MesPCl_2$ (0.29 mL, 3.32 mmol) (Mes = 2,4,6-$Me_3C_6H_2$-) were added via syringe. The solution immediately turned yellow with warming. After 18 h of stirring, all volatile materials were removed under reduced pressure, and the resulting yellow solid was extracted with warm toluene (40 mL). The solution was filtered twice through Celite and concentrated to *ca*. 10 mL. Slow cooling yielded a yellow oil (0.40 g) which was identified spectroscopically as a *cis*/*trans* mixture (1:2) of the diazadiphosphetidine $(MesPNPh)_2$ (**8**) (0.83 mmol, 50% based on phosphorus): ^1H NMR (300 MHz, C_6D_6) δ 7.08 (t, $J = 8.1$ Hz, 4H, *m*-H, Ph), 6.90−6.68 (m, 13H), 6.56 (s, 4H, *m*-H, Mes), 2.49 (s, 6H, CH_3), 2.43 (s, 12H, CH_3), 2.19 (s, 3H, CH_3), 2.00 (s, 6H, CH_3); ^{31}P NMR (300 MHz, C_6D_6) δ 220.4 (t, $^2J_{PP} = 30.2$ Hz, *cis* isomer), 196.6 (d, $^2J_{PP} = 26.5$ Hz, *trans* isomer).

$(GeNPh)_4$ (9). $GeCl_2$·dioxane (0.93 g, 4.0 mmol) was dissolved in THF (30 mL), and 1,4-dioxane (1 mL, 11.7 mmol) was added via syringe. ((THF)$MgNPh)_6$ (0.75 g, 0.67 mmol) was then added slowly via a solids-addition tube, after which the orange solution was heated to reflux for 14 h. The solution was then filtered through a frit, and all volatile materials were removed under reduced pressure. The resulting dark yellow oil was dissolved in toluene (10 mL), and the solution was concentrated to *ca*. 5 mL. Cooling to −20 °C yielded large pale yellow plates of $(GeNPh)_4$ (**9**) (0.20 g, 0.31 mmol, 31% based on germanium): mp 214−215 °C; ^1H NMR (300 MHz, C_6D_6) δ 7.19 (d, $J = 7.2$ Hz, 2H, *o*-H), 7.12 (t, $J = 6.9$ Hz, 2H, *m*-H), 6.88 (t, 7.2 Hz, 1H, *p*-H); ^{13}C NMR (300 MHz, C_6D_6) δ 150.1 (s, ipso-C), 130.0 (d, *o*-C), 122.8 (d, *p*-C), 121.6 (d, *m*-C); IR (Nujol) ν 1595 (s), 1490 (s), 1375 (mw), 1260 (sh, ms), 1220 (br, ms), 1100 (br, ms), 1030 (ms), 805 (s), 690 (sh, ms), 450 (br, m) cm^{-1}.

$[(SnNPh)_4\cdot\{MgCl_2(THF)_4\}]_\infty$ (10). ((THF)$MgNPh)_6$ (0.75 g, 0.67 mmol) was dissolved in THF (40 mL). Dioxane (1 mL, 11.7 mmol) was added via syringe. $SnCl_2$ (0.76 g, 4.0 mmol) was then added via a solids-addition tube, and the solution was heated to *ca*. 50 °C for 14 h. The solvent was removed under reduced pressure, and the residue was extracted with toluene (50 mL). After filtration through a frit, the solution was concentrated to incipient crystallization under reduced pressure. Cooling to −20 °C yielded small, pale, yellow crystals. Recrystallization from THF/toluene (1:1) afforded colorless needles of $[(SnNPh)_4\cdot\{MgCl_2(THF)_4\}]_\infty$ (**10**) (0.38 g, 0.31 mmol, 31% based on tin): mp 310 °C dec; ^1H NMR (300 MHz, C_6D_6) δ 7.17 (t, $J = 7.6$ Hz, 2H, *m*-H), 6.94 (d, $J = 7.5$ Hz, 2H, *o*-H), 6.84 (t, $J = 7.4$ Hz, 1H, *p*-H), 3.64 (s, 4H, THF), 1.37 (s, 4H, THF); IR (Nujol) ν 1580 (w), 1260 (s), 1215 (w), 1095 (br, s), 1020 (s), 800 (s), 680 (w) 565 (br, w) cm^{-1}.

$(SnNPh)_4$·0.5PhMe (11). ((THF)$MgNPh)_6$ (0.75 g, 0.67 mmol) was dissolved in THF (20 mL), and 1,4-dioxane (2 mL, 23 mmol) was added via syringe. Then $SnCl_2$ (0.76 g, 4.0 mmol) was added via a solids-addition tube, and the solution was heated to reflux for 18 h. The solvent was removed under reduced pressure, and the yellow residue was extracted into hot (*ca*. 70 °C) toluene (40 mL). The solution was filtered through a frit and concentrated to *ca*. 5 mL. Cooling to −20 °C yielded small, yellow crystals. Recrystallization from toluene afforded fine yellow needles of $(SnNPh)_4$·0.5PhMe (**11**) (0.35 g, 0.42

---

[7] Gottardi, W. *Monatsh. Chem.* **1973**, *104*, 1681.

[8] Oshikawa, T.; Yamashita, M.; *Chem. Ind.* (*Tokyo*) **1985**, 126.

[9] Fjeldberg, T.; Haaland, A.; Schilling, B. E. R.; Lappert, M. F.; Thorne, A. J. *J. Chem. Soc., Dalton Trans.* **1986**, *8*, 1551.

[10] Pauly, W. *Justus Liebigs Ann. Chem.* **1877**, *187*, 199. *Beilstein* **1929**, *12*, 201.

[11] Knoevenagel, H. *J. Prakt. Chem.* **1914**, *89*, 50. *Beilstein* **1934**, *16*, 310.

[12] Kirch, K.; Riesser, P.; Knock, F. *Chem. Ber.* **1991**, *124*, 1143.

[13] Davies, A. R.; Dronsfield, A. T.; Hazeldine, R. N. *J. Chem. Soc., Perkin Trans.* **1973**, *1*, 379.

Table 1. Selected Crystallographic and Refinement Data for **2**, **3**, **9**, **10**, and **14**[a]

	2	**3**	**9**	**10**	**14**
formula	$C_{93}H_{108}Mg_6N_6O_{7.25}$	$C_4H_9Br_2N$	$C_{24}H_{20}Ge_4N_4$	$C_{40}H_{52}Cl_2MgN_4O_4Sn_4$	$C_{86}H_{154}Mg_6N_{24}O_6P_6$
M_r	1587.5	230.9	6548	1222.83	1952.02
a, Å	28.101(7)	6.682(2)	10.749(2)	12.770(3)	22.478(4)
b, Å	35.851(7)	10.834(3)	12.358(3)	13.554(3)	16.339(3)
c, Å	36.816(7)	11.080(3)	35.818(7)	25.839(5)	29.387(6)
α, deg		66.25(2)			
β, deg		89.88(2)			
γ, deg		82.53(2)			
V, Å^3	37091(14)	726.9(3)	4758(2)	4472(2)	10793(4)
Z	2	4	8	4	4
space group	*Fddd*	$P\bar{1}$	*Pbca*	$P2_12_12_1$	*Pbcn*
λ, Å	1.541 78	0.710 73	1.541 78	1.541 78	1.541 78
d(calc), g cm^{-3}	1.251	2.110	1.828	1.816	1.201
μ, mm^{-1}	0.995	11.045	5.990	19.143	1.733
no. of reflns with $I > 2\sigma(I)$	3500	2043	2981	3190	4696
no. of paramtrs refnd	584	135	289	256	644
R^b	0.068	0.038	0.040	0.040	0.081
R_w	0.090	0.044	0.108	0.101	0.173
GOF	1.31	0.74	1.097	1.070	1.060

[a] Data collections were carried out at 130 K. [b] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$; $R_w = \sum(|F_o| - |F_c|)\sqrt{w}/\sum|F_o|\sqrt{w}$.

mmol, 42% based on tin): mp 91−92 °C dec; ^{1}H NMR (300 MHz, C_6D_6) δ 7.18 (t, $J = 7.5$ Hz, 2H, *m*-H), 6.94 (d, $J = 7.5$ Hz, 2H, *o*-H), 6.84 (t, $J = 7.5$ Hz, 1H, *p*-H); ^{13}C NMR (300 MHz, C_6D_6) δ 153.9 (s, ipso-C), 129.8 (d, *m*-C), 120.9 (d, *o*-C), 120.6 (d, *p*-C); IR (Nujol) ν 1585 (s), 1480 (s), 1260 (m), 1215 (br, s), 1150 (w), 1100 (m), 1075 (ms), 1030 (ms), 995 (sh, w), 880 (ms), 840 (s), 810 (br, m), 760 (s), 735 (mw), 690 (s), 630 (m), 575 (br, ms), 430 (br, ms) cm^{-1}. Anal. Calcd for $C_{27.5}H_{24}N_4Sn_4$: C, 37.31; H, 2.73; N, 6.32. Found: C, 36.34; H, 2.91; N, 6.09.

$(PbNPh)_4 \cdot 0.5PhMe$ (12). ((THF)MgNPh)$_6$ (0.75 g, 0.67 mmol) was dissolved in THF (40 mL), and 1,4-dioxane (1 mL, 11.7 mmol) was added via syringe. $PbCl_2$ (1.12 g, 4.0 mmol) was added via a solids-addition tube. The solution was then refluxed for 18 h, whereupon the solvent was removed under reduced pressure the resulting orange residue was dissolved in hot toluene (50 mL), and the solution was quickly filtered. Cooling the solution to ambient temperature yielded fine orange crystals of $(PbNPh)_4 \cdot 0.5PhMe$ (**12**) (0.53 g, 0.27 mmol, 40% based on lead): mp 278 °C dec; ^{1}H NMR (300 MHz, C_6D_6) δ 7.49 (t, $J = 7.2$ Hz, 2H, *m*-H), 6.66 (t, $J = 7.4$ Hz, 1H, *p*-H), 6.23 (d, $J = 7.4$ Hz, 2H, *o*-H); IR (Nujol) ν 1575 (ms), 1260 (mw), 1215 (vs), 1180 (w), 1150 (w), 1100 (w, br), 1070 (mw), 1020 (m), 990 (sh, w), 835 (m), 800 (br, m), 760 (sh, ms), 730 (w), 690 (m), 560 (w), 410 (w), 385 (w) cm^{-1}. Anal. Calcd for $C_{27.5}H_{24}N_4Pb_4$: C, 26.65; H, 1.95; N, 4.52. Found: C, 26.81; H, 2.06; N, 4.19.

$(Ph_3POMgNPh)_6$ (13). ((THF)MgNPh)$_6$ (**1**) (0.30 g, 0.27 mmol) was dissolved in toluene (30 mL). Triphenylphosphine oxide (0.45 g, 1.62 mmol) was added via a solids-addition funnel, and the solution was refluxed for 18 h. The yellow solution was then filtered through Celite and concentrated to *ca*. 10 mL. After layering with hexane (5 mL), the solution was cooled in a −20 °C freezer overnight to yield triphenylphosphine oxide (0.10 g). The remaining solution was pumped to dryness under reduced pressure to yield a dark yellow oil. ^{31}P NMR (300 MHz, C_6D_6) spectroscopy of this oil gave a minor resonance peak at $\delta = 25.1$ (Ph_3PO) and a major (>90%) peak at $\delta = 35.0$ ((Ph$_3$POMgNPh)$_6$ (**13**), *ca*. 25% based on P).

$\{(Me_2N)_3POMgNPh\}_6 \cdot 2PhMe$ (14). ((THF)MgNPh)$_6$ (1.00 g, 0.88 mmol) was dissolved in toluene (40 mL). Hexamethylphosphorylamide (0.93 mL, 5.33 mmol) was added via syringe and the solution heated to reflux for 4.5 h. The solution was filtered through Celite. Slow cooling of the solution to room temperature yielded colorless crystals of $\{(Me_2N)_3POMgNPh\}_6 \cdot 2PhMe$ (**14**) (0.55 g, 0.32 mmol, 36%): mp 240 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 6.95 (t, $J = 8.4$ Hz, 2H, *m*-H), 6.86 (d, $J = 8.4$ Hz, 2H, *o*-H), 6.32 (t, $J = 6.6$ Hz, 1H, *p*-H), 2.35 (s, $J_{P-H} = 9.6$ Hz, 18H, NMe): ^{13}C NMR (300 MHz, C_6D_6) δ 172.10 (s, ipso-C), 127.54 (d, *m*-C), 127.14 (d, *o*-C), 105.86 (d, *p*-C), 36.73 (q, $J_{P-C} = 4.5$ Hz, NMe); ^{31}P NMR (300 MHz, C_6D_6) δ 21.75 ($J_{P-H} = 9.6$ Hz); IR (Nujol) ν 1570 (m), 1450 (s), 1300 (br, ms), 1200 (br, s), 1070 (sh, m), 970 (br, s), 855 (sh, m), 830 (sh, m), 745 (s), 690 (sh, s), 560 (br, ms), 450 (br, ms) cm^{-1}.

$(Ph_2SOMgNPh)_6$ (15). ((THF)MgNPh)$_6$ (0.87 g, 0.77 mmol) was dissolved in toluene (60 mL). Diphenyl sulfoxide (0.94 g, 4.6 mmol) was added via a solids-addition funnel. The initial yellow precipitate dissolved when the solution was heated to reflux. After refluxing for 16 h, the solution was filtered through Celite. The dark yellow solution was concentrated to *ca*. 15 mL and layered with hexane (5 mL). Slow cooling in a −20 °C freezer yielded a dark orange oil (*ca*. 0.40 g). This was identified spectroscopically as (Ph$_2$SOMgNPh)$_6$ (**15**) (0.21 mmol, 27%). Further attempts to crystallize this oil were unsuccessful: ^{1}H NMR (300 MHz, C_6D_6) δ 7.25 (m, 4H), 7.08 (m, 5H), 6.96 (m, 3H), 6.79 (t, $J = 7.6$ Hz, 2H), 6.53 (t, $J = 7.6$ Hz, 1H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 145.2 (s, ipso-C, NPh), 142.5 (s, ipso-C, SPh), 132.2 (d, *o*-C, SPh), 130.2 (d, *m*-C, SPh), 128.9 (d, *m*-C, NPh), 126.2 (d, *p*-C, SPh), 120.9 (d, *p*-C, NPh), 116.2 (d, *o*-C, NPh).

Alternative Synthesis of $((THF)Mg)_6(NPh)_4Br_4$ (16). ((THF)MgNPh)$_6$ (**1**) (0.75 g, 0.66 mmol) was dissolved in a diethyl ether/THF solution (4:1, 50 mL), and $MgBr_2$ (0.36 g, 2.0 mmol) was added via a solids-addition funnel. The solution was stirred for 12 h and then refluxed for a further 16 h. The solvent was removed under reduced pressure and the resulting residue extracted with toluene (30 mL). The solution was filtered through a pad of Celite and then concentrated to *ca*. 10 mL and layered with hexane (2 mL). Slow cooling in a −20 °C freezer yielded large colorless crystals of ((THF)Mg)$_6$(NPh)$_4$Br$_4$ (**16**) (0.57 g, 0.45 mmol, 69% based on magnesium): mp (does not melt <325 °C); ^{1}H NMR (300 MHz, C_6D_6) δ 7.42 (d, $J = 7.8$ Hz, 2H, *o*-H), 7.17 (t, $J = 7.2$ Hz, 2H, *m*-H), 6.69 (t, $J = 6.9$ Hz, 1H, H4), 4.02 (s, 6H, OCH$_2$), 1.22 (s, 6H, CH$_2$); ^{13}C NMR (300 MHz, C_6D_6) δ 165.5 (s, ipso-C), 129.1 (d, *o*-C), 124.7 (d, *m*-C), 113.2 (d, *p*-C), 71.5 (t, OCH$_2$), 25.2 (t, CH$_2$). These spectra were identical to those of an authentic sample prepared from $PhNH_2$ and EtMgBr.[3]

Alternative Synthesis of $((THF)MgNPh)_6$ (1). ((THF)Mg)$_6$(NPh)$_4$Br$_4$ (**16**) (1.50 g, 1.2 mmol) was dissolved in diethyl ether (80 mL). Dioxane (0.4 mL, 4.8 mmol) was added, and the solution was stirred for 16 h. The solution was filtered through a pad of Celite and then concentrated to incipient crystallization. Cooling in a −20 °C freezer yielded very fine crystals of ((THF)MgNPh)$_6$ (**1**) (0.81 g, 0.90 mmol, 60% based on magnesium). This product was shown to be identical spectroscopically to the previously reported ((THF)MgNPh)$_6$ (**1**) prepared by the reaction of $MgBu_2$ with aniline in THF.[6]

X-ray Crystallography. Crystals of **2**, **3**, **9**, **10**, or **14** were coated with hydrocarbon oil. Suitable crystals for data collection were selected and then mounted in the cold stream (130 K) of the diffractometer. Data for **2** were collected on a Siemens P4/RA diffractometer employing nickel-monochromated Cu Kα ($\lambda = 1.541\,78$ Å) radiation and operating at 15 kW. Data for **3** were collected as a Siemens R3m/V diffractometer employing graphite-monochromated Mo Kα ($\lambda = 0.710\,73$ Å) radiation and operating at 2 kW. Data for **9**, **10**, and **14** were collected on a Syntex P2$_1$ diffractometer employing graphite-monochromated Cu Kα ($\lambda = 1.541\,78$ Å) radiation and operating at 2 kW.

Table 2. Selected Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for Compounds **2**, **3**, **9**, **10**, and **14**

	x	*y*	*z*	*U*(eq)[a]		*x*	*y*	*z*	*U*(eq)[a]
Compound **2**									
Mg(1)	4180(1)	1114(1)	3547(1)	31(1)	C(6)	4766(2)	822(2)	4366(2)	28(2)
Mg(2)	4179(1)	2081(1)	3554(1)	32(1)	C(7)	5076(2)	1005(2)	4123(2)	31(2)
Mg(3)	3596(1)	1592(1)	3142(1)	31(1)	C(8)	5561(2)	957(2)	4133(2)	42(2)
N(1)	4042(2)	1099(1)	4086(1)	31(2)	C(9)	5761(2)	720(2)	4402(2)	56(3)
N(2)	4319(2)	1598(1)	3270(1)	32(2)	C(10)	5476(2)	551(2)	4645(2)	60(3)
N(3)	3458(2)	2086(1)	3398(1)	32(2)	C(11)	4701(2)	1561(2)	3040(2)	35(2)
C(1)	4254(2)	871(2)	4348(2)	33(2)	C(21)	3220(2)	2361(2)	3210(2)	34(2)
C(2)	3985(2)	680(2)	4609(2)	34(2)	O(1)	4558(2)	659(1)	3401(1)	44(2)
C(3)	4195(2)	465(2)	4878(2)	47(3)	O(2)	4584(1)	2511(1)	3386(1)	41(2)
C(4)	4677(2)	417(2)	4906(2)	57(3)	O(3)	3450(2)	1643(1)	2606(1)	40(2)
C(5)	4973(2)	596(2)	4640(2)	46(3)					
Compound **3**									
Br(1)	4467.2(10)	1381.6(6)	3700.7(6)	30.0(3)	Br(4)	4309.9(11)	2681.9(7)	−24.4(7)	24.7(3)
Br(2)	3130.9(11)	4458.5(7)	2179.2(7)	23.6(3)	Br(5)	8279.8(11)	1649.3(7)	−943.9(7)	36.3(3)
Br(3)	3639(6)	2678(4)	759(5)	27.0(11)	Br(6)	6520(6)	4662(5)	−2028(4)	27.0(11)
N(1)	2583(7)	2709(5)	2316(5)	19(2)	N(2)	5826(8)	2919(5)	−1563(5)	25(2)
C(1)	438(9)	2460(6)	2643(6)	24(2)	C(5)	4671(10)	2675(7)	−2613(6)	28(2)
C(2)	239(11)	1058(7)	2684(7)	33(3)	C(6)	2792(10)	3762(7)	−3042(7)	34(3)
C(3)	−876(10)	3556(7)	1453(7)	32(3)	C(7)	6055(13)	2940(8)	−3779(7)	41(3)
C(4)	−133(11)	2560(8)	3931(6)	33(3)	C(8)	4071(13)	1272(7)	−2139(8)	41(3)
Compound **9**									
Ge(1)	2201(1)	9252(1)	4174(1)	25(1)	N(3)	691(4)	9606(3)	3859(1)	23(1)
Ge(2)	1501(1)	9425(1)	3361(1)	25(1)	N(4)	2935(4)	8866(3)	3676(1)	23(1)
Ge(3)	−119(1)	8121(1)	3887(1)	24(1)	C(1)	1607(5)	7124(4)	4472(2)	28(1)
Ge(4)	2418(1)	7277(1)	3671(1)	25(1)	C(7)	318(5)	7404(4)	3101(1)	25(1)
N(1)	1502(4)	7725(3)	4132(1)	24(1)	C(13)	−112(5)	10482(4)	3967(2)	25(1)
N(2)	888(4)	7872(3)	3426(1)	24(1)	C(19)	4150(5)	9195(4)	3564(2)	27(1)
Compound **10**									
Sn(1)	2170(1)	−1359(1)	5817(1)	10(10)	N(4)	2808(8)	965(7)	6597(4)	7(2)
Sn(2)	3619(1)	−402(1)	6805(1)	10(10)	C(1)	4606(9)	−724(8)	5685(5)	7(3)
Sn(3)	1199(1)	377(1)	6667(1)	11(1)	C(7)	1779(10)	−1830(9)	6997(5)	12(3)
Sn(4)	2987(1)	933(1)	5737(1)	10(10)	C(13)	672(9)	457(9)	5472(5)	11(3)
Mg(1)	2843(3)	−352(3)	3756(2)	12(1)	C(19)	3131(10)	1875(9)	6850(5)	11(3)
Cl(1)	2690(2)	−546(2)	4712(1)	17(1)	O(1)	3240(7)	−1840(7)	3679(4)	16(2)
Cl(2)	2951(3)	−169(2)	2806(1)	21(1)	O(2)	1295(7)	−750(7)	3672(4)	19(2)
N(1)	3643(8)	−516(7)	5933(4)	9(2)	O(3)	4420(7)	3(7)	3842(4)	19(2)
N(2)	2059(8)	−1024(7)	6680(4)	8(2)	O(4)	2374(7)	1128(7)	3844(4)	21(2)
N(3)	1490(8)	137(7)	5816(4)	10(2)					
Compound **14**									
Mg(1)	852(1)	5531(1)	−301(1)	19(1)	O(2)	703(2)	3685(2)	1114(1)	41(1)
O(1)	1629(2)	5868(2)	−547(2)	34(1)	P(2)	1071(5)	3086(8)	1379(4)	30(2)
P(1)	2181(1)	6171(1)	−763(1)	31(1)	N(8)	−351(2)	5126(3)	759(2)	20(1)
N(1)	2779(2)	5642(4)	−658(2)	61(2)	C(19)	−623(3)	5329(3)	1161(2)	23(1)
N(2)	2125(3)	6122(4)	−1313(2)	53(2)	Mg(3)	190(1)	6031(1)	493(1)	19(1)
N(3)	2308(3)	7097(4)	−597(2)	62(2)	O(3)	278(2)	6937(2)	929(1)	27(1)
N(4)	897(2)	5226(3)	378(2)	21(1)	P(3)	381(1)	7650(1)	1226(1)	28(1)
C(7)	1469(2)	5201(4)	540(2)	24(1)	N(12)	171(2)	6398(3)	−182(2)	20(1)
Mg(2)	346(1)	4308(1)	617(1)	21(1)	C(31)	185(2)	7218(4)	−264(2)	22(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

The structure of **2** was solved in space group *Fddd* using direct and difference Fourier methods, developed, and refined routinely.[14] Disorder was observed for one of the solvent THF molecules. It was refined using partial occupancies of 56.7% for C(52), C(53), C(54) and 43.3% for C(52B), C(53B), C(54B). There is also a disordered THF molecule located on a special position (0.625, 0.125, *z*). The atoms are labeled C(S2) and C(S3); 25% of the molecule is present in the asymmetric unit. Hydrogen atoms were added geometrically and refined using a riding model with fixed thermal parameters equal to 0.05 Å^2. An absorption correction (XABS)[15] was applied. Refinement was by full-matrix least-squares methods based on *F*, with anisotropic parameters for all non-hydrogen atoms. The final difference map showed no features greater than 0.94 and −0.29 e Å^{-3}.

The structure of **3** was solved in space group $P\bar{1}$ using Patterson and difference methods.[14] There are two molecules in the asymmetric unit which pack, along with two symmetrically equivalent molecules, in a square arrangement around a center of symmetry. This gives rise to an unusual disorder in which the bromine atoms positions are interchanged with "lone-pair" positions in a ratio of 84.5(2)% and 15.5(2)%. Thus, of the four bromine atoms in the asymmetric unit, two are fully present, two are at 0.845 occupancy, and two are in the alternative at 0.155 occupancy. The last two bromines were refined with their isotropic thermal parameters linked together. The other four were refined with their thermal parameters free. Hydrogen atoms were added as rigid groups, assuming C−H of 0.96 Å, and refined by use of a riding model and fixed isotropic thermal parameters equal to 0.030 Å^2. An absorption correction (XABS)[15] was applied. In the final cycles of refinement, all non-hydrogen atoms were refined anisotropically except for the minor bromines. The largest peak in the difference map had a value 0.67 e Å^{-3}, adjacent to Br(4).

---

(14) Sheldrick, G. M. *SHELXTL-PLUS*: *A Program for Crystal Structure Determination*; Version 4.2; Siemens Analytical X-ray Instruments: Madison, WI, 1990.

(15) Program XABS provides an empirical correction based on F_o and F_c differences: H. Hope and B. Moezzi, Department of Chemistry, University of California, Davis.

The structure of **9** was solved in space group *Pbca* using direct and difference Fourier methods.[16] The initial solution located all non-hydrogen atoms. Hydrogen atoms were added in calculated positions, with C−H equal to 0.95 Å, and refined using a riding model with fixed thermal parameters equal to 0.05 $Å^2$. An absorption correction (XABS2)[17] was applied. Refinement was by full-matrix least-squares methods based on F^2, with anisotropic parameters for all non-hydrogen atoms. The final difference map showed no features greater than 0.673 and −1.054 e $Å^{-3}$.

The structure of **10** was solved in space group $P2_12_12_1$ using direct and difference Fourier methods.[16] The initial solution located a partial structure, and the remaining non-hydrogen atoms were located in a subsequent difference map. Hydrogen atoms were added in calculated positions and refined using a riding model with fixed thermal parameters equal to 0.05 $Å^2$. An absorption correction (XABS2)[17] was applied. Refinement was by full-matrix least-squares methods based on F^2, with anisotropic parameters for all Sn, Mg, and Cl atoms. The final difference map showed no features greater than 0.922 and −0.774 e $Å^{-3}$.

The structure of **14** was solved in space group *Pbcn* using direct and difference Fourier methods,[16] developed, and refined routinely. The structure shows two disorder problems which were sufficiently modeled with split occupancies. The $P(NMe_2)_3$ group involving atoms between P(2) and C(18) showed rotational disorder and was modeled with split occupancies of 53.3(8)% for P(2) to C(18) and 46.7(8)% for P(2A) to C(18A). The toluene solvent molecule was found to be disordered on two partially overlapping positions and refined isotropically with 63.2(12)% occupancy for C(37) to C(43) and 37.8(12)% occupancy for C(44) to C(50). The aromatic ring of the toluene molecule was constrained as a rigid hexagon. Hydrogen atoms were added geometrically and refined by use of a riding model and fixed isotropic thermal parameters equal to 0.05 $Å^2$. An absorption correction (XABS2)[17] was made. Refinement was by full-matrix least-squares methods based on F^2, with anisotropic thermal parameters for all non-hydrogen atoms except those of the toluene solvent molecule. The final difference map showed no features greater than 0.571 and −0.316 e $Å^{-3}$.

Results and Discussion

The magnesium imide $((THF)MgNPh)_6$ (**1**) was originally synthesized (eq 1) by the reaction between $MgEt_2$ and H_2NPh.[4] A more convenient route, however, involves the use of the readily available dibutylmagnesium (supplied commercially as a 1:1 mixture of *n*-butyl and *sec*-butyl groups in heptane solvent) instead of $MgEt_2$. This affords the product **1** in 84% yield.[6] The slightly more crowded 1-naphthyl derivative $\{(THF)MgN(1\text{-naphthyl})\}_6 \cdot 2.25THF$ (**2**) can be synthesized by the same method, and its hexameric structure (Figure 1) is very similar to that originally reported for **1** in spite of the larger size of the nitrogen substituent. At present, homometallic magnesium imide structures are confined to these two aryl derivatives and to species which may be in equilibrium with "$ArN(MgX)_2$" in solution, i.e. $((THF)Mg)_6(NPh)_4Br_4$. The only other instance of the involvement of a magnesium atom in an imide cage structure concerns the compound $\{HAlN(t\text{-Bu})\}_3\{N(t\text{-Bu})\}\{MgTHF\}$, in which one of the AlH corners is replaced by a Mg(THF) moiety.[18] The Mg−N distance 2.09 Å in this species and those found in **1** and **2** are very similar.

An interesting aspect of the double deprotonation of primary amines by electropositive main group 1 or 2 elements is that it has only been authenticated structurally for a few aromatic amine derivatives such as **1**, **2**, **16**, and **17** and $[\{(1\text{-naphthyl})NLi_2\}]_{10}(Et_2O)_6] \cdot Et_2O$ (**17**).[19] Apparently, the acidity[20] of the arylamines readily permits the generation of the imides whereas the less acidic alkylamines have not yet yielded readily characterizable products other than the less novel intermediate amide derivatives. In the case of the structure of $[\{(1\text{-naphthyl})NLi_2\}_{10}(Et_2O)_6] \cdot Et_2O$ (**17**), the $N_{10}Li_{14}$ core consists of two rhombic dodecahedra sharing a common face.[19] In contrast to **2**, it was obtained by double deprotonation of 1-naphthylamine with *n*-BuLi.

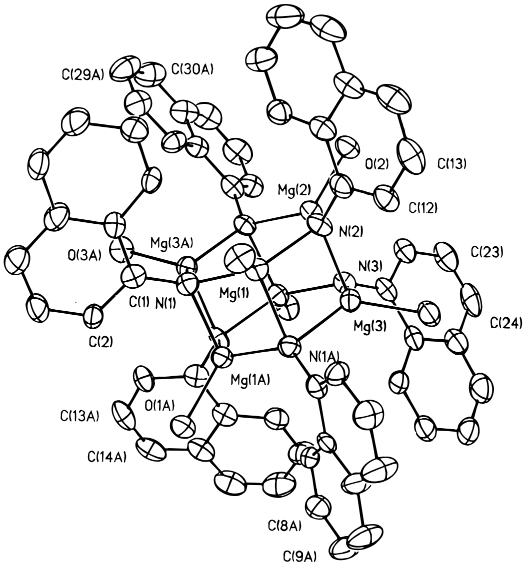


Figure 1. Thermal ellipsoid plot (30%) of **2**. For clarity, neither solvating THF carbons nor hydrogen atoms nor any atoms of the THF molecules of crystallization are shown.

The structure of **2** as shown in Figure 1 has a crystallographically imposed center of symmetry. The central Mg_6N_6 framework consists of a slightly distorted hexagonal prism containing alternating magnesium and nitrogen atoms. Each magnesium is solvated by a single THF molecule whereas each nitrogen bears a naphthyl group. As found for the structure of **1**, the Mg−N distances within the hexagonal rings (2.05 Å average) are slightly shorter than those which join the rings (2.09 Å average).[4] These Mg−N distances are similar to those observed for **1**, as are the Mg−N−Mg (117.6(2)°) and N−Mg−N (121.5(2)°) angles. Similarly, both the Mg−O (2.02 Å average) and N−C (1.38 Å average) distances are also comparable to those found for **1**.

The synthetic utility of the magnesium imide $((THF)MgNPh)_6$ (**1**) as an imide transfer agent has only been demonstrated in the case of a few reactions with some early metal cyclopentadienyl derivatives. For example, when **1** was treated with $(\eta^5\text{-}C_5H_5)TiCl_3$, the bridged titanium imide $\{(\eta^5\text{-}C_5H_5)Ti(Cl)(NPh)\}_2$ was obtained in good yield.[6] A much greater range of reactions, summarized in Scheme 1, is now discussed here.

Reaction between **1** and benzophenone proceeded in a clean, straightforward manner to give the expected triphenylimine product, $Ph_2C{=}NPh$ (**4**), in good isolated yield. A similar reaction between **1** and the nitroso compound $4\text{-}Me_2N(C_6H_4)NO$ gave the azo compound $4\text{-}Me_2N(C_6H_4)N{=}NPh$ (**5**) also in good yield. Diimine compounds could also be synthesized via the reaction of **1** with alkyldibromoamines. Treatment of **1** with the alkyldibromoamine $t\text{-}BuNBr_2$ (**3**) gave the expected diimine product $t\text{-}BuN{=}NPh$ (**6**). The yield of this reaction was only 27%, however. This is probably a consequence of the fact that

---

(16) *SHELXTL-PLUS*: *A Program for Crystal Structure Determination*, Version 5.02; Siemens Analytical X-ray Instruments: Madison, WI, 1994.

(17) Parkin, S. R.; Moezzi, B.; Hope, H. XABS2: an empirical absorption correction program. *J. Appl. Crystallogr.* **1995**, *28*, 53.

(18) Del Piero, G.; Cesari, M.; Cucinella, S.; Mazzei, A. *J. Organomet. Chem.* **1977**, *137*, 265.

(19) Armstrong, D. R.; Barr, D.; Clegg, W.; Drake, S. R.; Singer, R. J.; Snaith, R.; Stalke, D.; Wright, D. S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1707.

(20) March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley: New York, 1992; p 250.

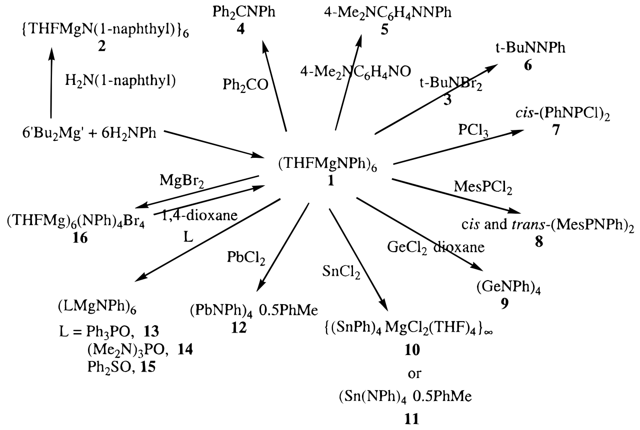
Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compounds **2**, **3**, **9**, **10**, and **14**

Compound **2**							
Mg(1)−N(1)	2.022(5)	Mg(2)−N(3)	2.105(5)	Mg(3)−O(3)	2.025(5)	N(1)−Mg(3A)	2.066(5)
Mg(1)−N(2)	2.053(5)	Mg(2)−O(2)	2.012(5)	Mg(3)−N(1A)	2.066(5)	N(2)−C(11)	1.373(8)
Mg(1)−O(1)	2.019(5)	Mg(2)−N(3A)	2.054(5)	N(1)−C(1)	1.397(8)	N(3)−C(21)	1.378(8)
Mg(1)−N(1A)	2.090(5)	Mg(3)−N(2)	2.084(5)	N(1)−Mg(1A)	2.090(5)	N(3)−Mg(2A)	2.054(5)
N(1)−Mg(1)−N(2)	123.2(2)	N(2)−Mg(2)−N(3A)	122.7(2)	Mg(1)−N(1)−C(1)	127.5(4)	Mg(1)−N(2)−C(11)	111.9(4)
N(1)−Mg(1)−O(1)	110.0(2)	N(3)−Mg(2)−N(3A)	95.0(2)	Mg(1)−N(1)−Mg(1A)	87.4(2)	Mg(2)−N(2)−C(11)	122.9(4)
N(2)−Mg(1)−O(1)	116.8(2)	O(2)−Mg(2)−N(3A)	113.7(2)	C(1)−N(1)−Mg(1A)	126.2(4)	Mg(3)−N(2)−C(11)	128.4(4)
N(1)−Mg(1)−N(1A)	92.5(2)	N(2)−Mg(3)−N(3)	94.1(2)	Mg(1)−N(1)−Mg(3A)	119.3(2)	Mg(2)−N(3)−Mg(3)	86.3(2)
N(2)−Mg(1)−N(1A)	95.1(2)	N(2)−Mg(3)−O(3)	114.6(2)	C(1)−N(1)−Mg(3A)	104.3(4)	Mg(2)−N(3)−C(21)	127.5(4)
O(1)−Mg(1)−N(1A)	115.3(2)	N(3)−Mg(3)−O(3)	109.4(2)	Mg(1A)−N(1)−Mg(3A)	84.8(2)	Mg(3)−N(3)−C(21)	118.7(4)
N(2)−Mg(2)−N(3)	93.0(2)	N(2)−Mg(3)−N(1A)	94.9(2)	Mg(1)−N(2)−Mg(2)	114.9(2)	Mg(2)−N(3)−Mg(2A)	85.0(2)
N(2)−Mg(2)−O(2)	112.3(2)	N(3)−Mg(3)−N(1A)	118.7(2)	Mg(1)−N(2)−Mg(3)	85.3(2)	Mg(3)−N(3)−Mg(2A)	118.8(2)
N(3)−Mg(2)−O(2)	117.1(2)	O(3)−Mg(3)−N(1A)	120.8(2)	Mg(2)−N(2)−Mg(3)	86.5(2)	C(21)−N(3)−Mg(2A)	114.1(4)
Compound **3**							
Br(1)−N(1)	1.941(4)	C(1)−C(2)	1.524(11)	Br(5)−N(2)	1.926(5)	N(2)−C(5)	1.525(10)
Br(2)−N(1)	1.923(6)	C(1)−C(4)	1.518(11)	Br(6)−N(2)	1.869(8)	C(5)−C(7)	1.540(10)
Br(3)−N(1))	1.874(8)	Br(4)−N(2)	1.925(6)				
Br(1)−N(1)−Br(2)	105.5(3)	Br(4)−N(2)−Br(5)	106.0(2)	Br(1)−N(1)−Br(3)	103.8(3)	Br(4)−N(2)−Br(6)	102.0(3)
Br(2)−N(1)−Br(3)	101.0(3)	Br(5)−N(2)−Br(6)	107.2(3)	Br(1)−N(1)−C(1)	110.3(3)	Br(44)−N(2)−C(5)	112.7(4)
Br(2)−N(1)−C(1)	113.7(4)	Br(5)−N(2)−C(5)	111.0(4)	Br(3)−N(1)−C(1)	121.0(5)	Br(6)−N(2)−C(5)	117.0(4)
Br(3)−Br(4)−N(2)	171.2(3)						
Compound **9**							
Ge(1)−N(4)	2.006(4)	Ge(2)−N(4)	2.032(4)	Ge(3)−N(1)	2.011(4)	Ge(4)−N(2)	2.005(4)
Ge(1)−N(3)	2.025(4)	Ge(2)−N(2)	2.042(4)	Ge(3)−N(3)	2.033(4)	Ge(4)−N(4)	2.042(4)
Ge(1)−N(1)	2.036(4)	Ge(3)−N(2)	1.999(4)	Ge(4)−N(1)	2.001(4)	N−C	1.433(7) (av)
Ge(2)−N(3)	1.997(4)						
N(4)−Ge(1)−N(3)	82.6(2)	N(2)−Ge(3)−N(1)	81.6(2)	Ge(4)−N(1)−Ge(3)	97.7(2)	Ge(2)−N(3)−Ge(1)	97.1(2)
N(4)−Ge(1)−N(1)	81.9(2)	N(2)−Ge(3)−N(3)	82.3(2)	Ge(4)−N(1)−Ge(1)	97.8(2)	Ge(2)−N(3)−ge(3)	97.5(2)
N(3)−Ge(1)−N(1)	82.1(2)	N(1)−Ge(3)−N(3)	82.6(2)	Ge(3)−N(1)−Ge(1)	97.2(2)	Ge(1)−N(3)−Ge(3)	96.9(2)
N(3)−Ge(2)−N(4)	82.7(2)	N(1)−Ge(4)−N(2)	81.7(2)	Ge(3)−N(2)−Ge(4)	97.9(2)	Ge(1)−N(4)−Ge(2)	96.6(2)
N(3)−Ge(2)−N(2)	82.1(2)	N(1)−Ge(4)−N(4)	81.9(2)	Ge(3)−N(2)−Ge(2)	97.1(2)	Ge(1)−N(4)−Ge(4)	97.5(2)
N(4)−Ge(2)−N(2)	82.1(2)	N(2)−Ge(4)−N(4)	82.8(2)	Ge(4)−N(2)−Ge(2)	97.4(2)	Ge(2)−N(4)−Ge(4)	96.6(2)
Compound **10**							
Sn(1)−N(3)	2.205(9)	Sn(3)−N(4)	2.210(10)	Mg(1)−O(1)	2.089(10)	N93)−C(13)	1.44(2)
Sn(1)−N(1)	2.221(10)	Sn(3)−N(3)	2.252(11)	Mg(1)−O(4)	2.106(10)	N(4)−C(19)	1.46(2)
Sn(1)−N(2)	2.278(10)	Sn(4)−N(1)	2.195(10)	Mg(1)−Cl(2)	2.471(5)	Sn(1)- - -Cl(1)	3.132(2)
Sn(2)−N(2)	2.188(10)	Sn(4)−N(3)	2.205(10)	Mg(1)−Cl(1)	2.491(5)	Sn(2)- - -Cl(2A)	3.363(2)
Sn(2)−N(4)	2.191(9)	Sn(4)−N(4)	2.234(10)	N(1)−C(1)	1.41(2)	Sn(3)- - -Cl(2A)	3.151(2)
Sn(2)−N(1)	2.258(10)	Mg(1)−O(2)	2.060(10)	N(2)−C(7)	1.41(2)	Sn(4)- - -Cl(1)	3.343(2)
Sn(3)−N(2)	2.193(10)						
N(3)−Sn(1)−N(1)	82.0(4)	N(1)−Sn(4)−N(4)	80.1(3)	O(3)−Mg(1)−Cl(2)	91.6(3)	Sn(1)−N(1)−Sn(2)	99.1(4)
N(3)−Sn(1)−N(2)	78.1(4)	N(3)−Sn(4)−N(4)	80.2(4)	O(1)−Mg(1)−Cl(2)	89.4(3)	Sn(2)−N92)−Sn(3)	97.2(4)
N(1)−Sn(1)−N(2)	79.6(4)	N(4)−Sn(4)−Sn(1)	85.6(2)	O(4)−Mg(1)−Cl(2)	91.5(3)	Sn(2)−N(2)−Sn(1)	99.5(4)
N(2)−Sn(2)−N(4)	81.9(4)	O(2)−Mg(1)−O(3)	178.2(4)	O(2)−Mg(1)−Cl(1)	90.1(3)	Sn(3)−N(2)−Sn(1)	100.9(4)
N(2)−Sn(2)−N(1)	80.7(4)	O(2)−Mg(1)−O(1)	88.3(4)	O(3)−Mg(1)−Cl(1)	89.7(3)	Sn(4)−N(3)−Sn(1)	96.2(4)
N(4)−Sn(2)−N(1)	79.6(4)	O(3)−Mg(1)−O(1)	89.9(4)	O(1)−Mg(1)−Cl(1)	90.7(3)	Sn(4)−N(3)−Sn(3)	99.3(4)
N(2)−Sn(3)−N(4)	81.3(4)	O(2)−Mg(1)−O(4)	89.3(4)	O(4)−Mg(1)−Cl(1)	88.4(3)	Sn(1)−N(3)−Sn(3)	101.3(4)
N(2)−Sn(3)−N(3)	78.9(4)	O(4)−Mg(1)−O(4)	92.5(4)	Cl(2)−Mg(1)−Cl(1)	178.7(2)	Sn(2)−N94)−Sn(3)	96.6(4)
N(4)−Sn(3)−N93)	79.6(4)	O(1)−Mg(1)−O(4)	177.4(4)	Sn(4)−N91)−Sn(1)	96.0(4)	Sn(2)−N(4)−Sn(4)	100.3(4)
N(1)−Sn(4)−N(3)	82.7(4)	O(2)−Mg(1)−Cl(2)	88.5(3)	Sn(4)−N(1)−Sn(2)	99.4(4)	Sn(3)−N(4)−Sn(4)	99.7(4)
Compound **14**[a]							
Mg(1)−O(1)	1.968(4)	N(4)−Mg(2)	2.068(5)	O(2)−P(2A)	1.48(2)	Mg(3)−O(3)	1.968(4)
Mg(1)−N(8)#1	2.056(5)	N(4)−Mg(3)	2.091(5)	O(2)−P(2)	1.50(2)	Mg(3)−N(12)	2.070(5)
Mg(1)−N(4)	2.061(5)	Mg(2)−O(2)	1.954(4)	N(8)−Mg(1)#1	2.056(5)	O(3)−P(3)	1.474(4)
Mg(1)−N(12)	2.115(5)	Mg(2)−N(12)#1	2.077(5)	N(8)−Mg(3)	2.067(5)	N(12)−Mg(2)#1	2.077(5)
O(1)−P(1)	1.479(4)						
N(8)#1−Mg(1)−N(4)	122.3(2)	Mg(2)−N(4)−Mg(3)	86.9(2)	P(2)−O(2)−Mg(2)	162.9(5)	N(8)−Mg(3)−N(4)	93.3(2)
N(8)#1−Mg(1)−N(12)	93.6(2)	N(4)−Mg(2)−N(12)#1	121.9(2)	Mg(1)#1−N(8)−Mg(3)	116.6(2)	N(12)−Mg(3)−N(4)	92.5(2)
N(4)−Mg(1)−N(12)	92.1(2)	N(4)−Mg(2)−N(8)	93.0(2)	Mg(1)#1−N(8)−Mg(2)	86.9(2)	P(3)−O(3)−Mg(3)	174.8(3)
P(1)−O(1)−Mg(1)	174.6(3)	N(12)#1−Mg(2)−N(8)	93.4(2)	Mg(3)−N(8)−Mg(2)	86.7(2)	Mg(3)−N(12)−Mg(1)	87.2(2)
Mg(1)−N(4)−Mg(2)	118.3(2)	P(2A)−O(2)−Mg(2)	176.0(6)	N(8)−Mg(3)−N(12)	123.9(2)	Mg(2)#1−N(12)−Mg(1)	86.0(2)

[a] Symmetry transformation used to generate equivalent atoms.

side reactions such as bromination of the aryl ring can also occur. The structure of the alkyldibromoamine *t*-BuNBr$_2$ is shown in Figure 2. It represents a relatively rare instance of a solid state structure featuring nitrogen bound to more than one halogen. The N−Br distances in **3** are in the range 1.869(8)−1.941(4) Å. These values are close to the sum (1.87 Å) of the covalent radii of nitrogen (0.73 Å) and bromine (1.14 Å). They are slightly longer than the 1.843(3) Å N−Br distance observed in *N*-bromobenzamide or the 1.817(7) Å seen in *N*-bromosuccinimide.[21] The difference may be due to the fact that in these

Scheme 1. Summary of the Reactions of ((THF)MgNPh)$_6$ (**1**)



molecules the nitrogens are sp^2 hybridized in contrast to the sp^3 hybridization observed in **3**. The nitrogen centers have pyramidal coordination with average interligand angles at N(1) and N(2) of 109.8 and 109.9°, respectively. These are only slightly greater than the value found for NH$_3$. This is surprising in view of the larger sizes of the substituents in **3**. However, it is probable that the electronegative bromines keep the interligand angles from becoming too wide since they tend to raise the inversion barrier at nitrogen.[22]

The reaction between **1** and 4 equiv of phosphorus trichloride led to the isolation of the diazadiphosphetidine *cis*-(PhNPCl)$_2$ (**7**). The presence of **7** was verified by a comparison of the crystallographic lattice parameters and the ^{31}P NMR data with those of the reported structure.[23] The reaction with MesPCl$_2$ (Mes = 2,4,6-Me$_3$C$_6$H$_2$) gave, however, a mixture of the cis/trans (1:2) diazadiphosphetidine product (MesPNPh)$_2$ (**8**) in good yield.[24,25] The isomers were not separated.

The reaction between **1** and the main group 4 dihalides GeCl$_2$·dioxane, SnCl$_2$, and PbCl$_2$ afforded the corresponding tetrameric metal imides in good to moderate yields. The reaction of **1** with GeCl$_2$·dioxane gave the germanium imide (GeNPh)$_4$ (**9**), whose structure is illustrated Figure 3. It possesses a distorted Ge$_4$N$_4$ cubane core consisting of alternating germanium and nitrogen atoms, each nitrogen being substituted by a phenyl ring. The N−Ge−N angles are less than 90° (82.2(2)° average), whereas the corresponding Ge−N−Ge angles are 97.3(2)° (average). The cubane structural type has not been structurally authenticated for germanium imides. Nonetheless the Ge$_4$N$_4$ core bears a close resemblance to Sn$_4$N$_4$ and Pb$_4$N$_4$ imido structures which are now well established.[26] The Ge−N bond distances are essentially equivalent and have an average length of 2.02(2) Å. This distance is longer than those reported for the related trimeric and dimeric imides [GeN(2,6-*i*-Pr$_2$C$_6$H$_3$)]$_3$ (1.86 Å)[27] and [GeN(2,4,6-*t*-Bu$_3$C$_6$H$_2$)]$_2$ (1.85 Å),[28] where the germaniums and nitrogens are two- and three-coordinate, respectively. The isolation of a tetrameric **9** instead of a dimeric or trimeric species illustrates the importance of steric effects in the determination of the structure of this class of compound.

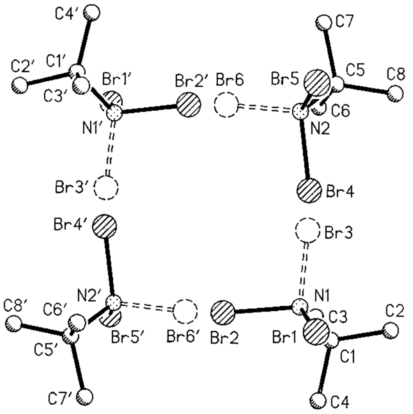


Figure 2. Thermal ellipsoid plot (30%) of the unit cell of **3** illustrating the structural disorder. Hydrogen atoms are not shown.

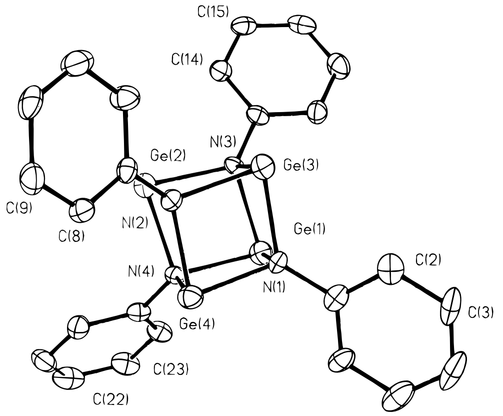


Figure 3. Thermal ellipsoid plot (30%) of **9**. Hydrogen atoms are not shown.

A similar reaction between **1** and SnCl$_2$ or PbCl$_2$ affords (SnNPh)$_4$ (**11**) or (PbNPh)$_4$ (**12**). Each of these compounds crystallizes with 0.5 equiv of PhMe per tetramer. Since the structures of other tetrameric Sn(II) and Pb(II) imides have already been reported,[26] it was decided not to determine their structures. Nonetheless the presence of a tetrameric (SnNPh)$_4$ was verified in the unusual structure observed for {(SnNPh)$_4$·MgCl$_2$(THF)$_4$}$_\infty$ (**10**) (Figure 4), which was isolated using a workup procedure different from that for **11**. The main structural motif in **10** consists of chains formed of alternating (SnNPh)$_4$ and MgCl$_2$(THF)$_4$ units. The halides act as bridges between the tin and magnesium centers; however, the Sn- - -Cl interactions are rather long (3.13−3.36 Å) so that the bridging is weak. Not surprisingly the Sn−N bond lengths, which average 2.22(2) Å, are similar to those previously reported for other tetrameric tin(II) imides.[26] The average Mg−Cl and Mg−O distances of 2.08(1) and 2.481(5) Å are well within the known range.[29]

It was also hoped that **1** would readily convert phosphine oxides to phosphinimines. However, when **1** was treated with the phosphine oxide Ph$_3$PO or (Me$_2$N)$_3$PO, the corresponding iminophosphorane, R$_3$P=NPh, was not formed even in the

---

(21) Jabay, O.; Pritzkow, H.; Jander, J. *Z. Naturforsch., B* **1977**, *32*, 1416.

(22) Lambert, J. B. In *Topics in Stereochemistry*; Allinger, N. L., Eliel, E. L., Eds.; Wiley: New York, 1971; Vol. 6, p 19.

(23) Chen, H.-J.; Haltiwanger, R. C.; Hill, T. G.; Thompson, M. L.; Coons, D. E.; Norman, A. D. *Inorg. Chem.* **1985**, *24*, 4725.

(24) Scherer, O. J.; Schnabl, G. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 772.

(25) Lehousse, C.; Haddad, M.; Barrans, J. *Tetrahedron Lett.* **1982**, *23*, 4171.

(26) For example: (a) Veith, M.; Sommer, M.-L.; Jäger, D. *Chem. Ber.* **1979**, *112*, 2581. (b) Veith, M.; Recktenwald, O. *Z. Naturforsch., B* **1983**, *34*, 1054. (c) Veith, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1. (d) Veith, M. *Coord. Chem. Rev.* **1990**, *90*, 1. (e) Chen, H.; Bartlett, R. A.; Dias, H. V. R.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1991**, *30*, 3390. (f) Allan, R. E.; Beswick, M. A.; Edwards, A. J.; Paver, M. A.; Rennie, M.-A.; Raithby, P. R.; Wright, D. S. *J. Chem. Soc., Dalton Trans.* **1995**, 1991.

(27) Bartlett, R. A.; Power, P. P. *J. Am. Chem. Soc.* **1990**, *112*, 3660.

(28) Hitchcock, P. B.; Lappert, M. F.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1990**, 1587.

(29) Holloway, C. E.; Melnik, M. *J. Organomet. Chem.* **1994**, *465*, 1.

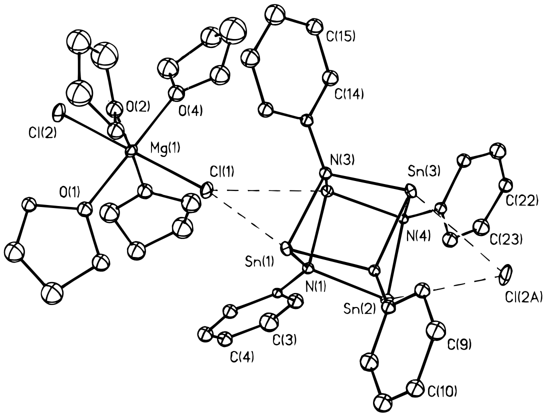


Figure 4. Thermal ellipsoid plot (30%) of **10** illustrating the association of the $(SnNPh)_4$ and $MgCl_2(THF)_4$ units. Hydrogen atoms are not shown.

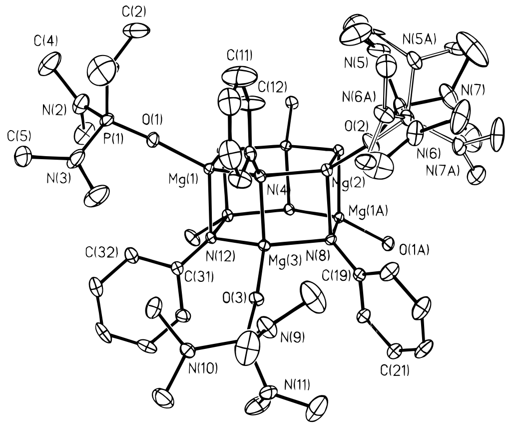


Figure 5. Thermal ellipsoid plot (30%) of **14** showing the disorder in one of the $(Me_2N_3)PO$ solvating molecules. Only oxygens and ipso-carbon atoms are shown for three of the $(Me_2N)_3PO$ and three of the phenyl donors. Hydrogen atoms are omitted for clarity.

refluxing solvent. Instead, substitution of the THF's took place and the adduct $\{(Ph_3PO)MgNPh\}_6$ (**13**) or $[\{(Me_2N)_3PO\}MgNPh]_6\cdot 2PhMe$ (**14**) was formed.

The structure of $[\{(Me_2N)_3PO\}MgNPh]_6\cdot 2PhMe$ (**14**) was determined and is shown in Figure 5. The Mg_6N_6 molecules are located on crystallographic centers of symmetry. As with **2**, the core of **14** consists of alternating magnesium and nitrogen atoms in an hexagonal prismatic cage. Each nitrogen bears a phenyl substituent, while the magnesiums are solvated through oxygen by a $(Me_2N)_3PO$ group. Though the Mg−N−Mg (117.3(2)°) and N−Mg−N (122.7(2)°) angles of the Mg_6N_6 cage are comparable to those of **1**,[4] the Mg−N distances within the hexagonal rings (2.07(1) Å average) and the Mg−N bonds linking the rings (2.10(1) Å average) show a slight lengthening with respect to those in **1** (2.05(1) and 2.08(1) Å, respectively). The average N−C distance (1.37(1) Å average), however, is the same as that found in **1**. The Mg−O distances (1.96(1) Å average) in **14** are significantly shorter (1.96(1) Å in **12** vs 2.04(1) Å in **1**). The P−O distances (1.48(1) Å average) are similar to those observed in other HMPA complexes, and the slight deviation from linearity of the Mg−O−P angles is not unusual[30] and has been observed in other HMPA metal complexes.

The ^{31}P NMR chemical shift of $[\{(Me_2N)_3PO\}MgNPh]_6$ (**14**) is *ca*. 3 ppm downfield from that in free $(Me_2N)_3PO$ (HMPA) ($\delta = 24.3$).[31] This is, of course, consistent with a slight reduction in the electron density at the phosphorus center owing to the complexation of the oxygen. A similar ^{31}P downfield shift was observed for **13** which was obtained when Ph_3PO was added to **1**. Formation of the adduct **14**, instead of the iminophosphorane $R_3P{=}NPh$, from the reaction of HMPA with **1** is consistent with a strong P=O bond. The robust nature of the P−O bond is also reflected in the fact that it often maintains its integrity in the presence of quite reactive substrates. For instance, it is possible to form stable HMPA complexes of aryllithium compounds[32] without the formation of coupled products.

Reaction of **1** with Ph_2SO also did not give the corresponding sulfinimide. The adduct $\{(Ph_2SO)MgNPh\}_6$ (**15**) was the only product isolated from this reaction. The reaction of **1** with $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ with the intention of converting metal-bound CO to PhNC (bound or unbound) did not result in any detectable reaction. Reaction between **1** and 3 equiv of $MgBr_2$ afforded 1.5 equiv of $((THF)Mg)_6(NPh)_4Br_4$ (**16**) (eq 4). It can be

$$\underset{\mathbf{1}}{((THF)MgNPh)_6} + 3MgBr_2 \rightarrow 1.5\underset{\mathbf{16}}{((THF)Mg)_6(NPh)_4Br_4} \quad (4)$$

demonstrated (^{13}C NMR and X-ray data) that this product is similar to the corresponding Et_2O-solvated compound previously crystallized[3] from "$PhN(MgBr)_2$" solutions. This Et_2O-solvated species has been shown to have an adamantyl Mg_6N_4 core with doubly deprotonated nitrogens.[3] It is probable that the THF-solvated **16** has a similar structure which, like the Et_2O-solvated analogue, results from disproportionation of the "$PhN(MgBr)_2$" species to give **16** and $MgBr_2$ as already shown in eq 2. Compound **16** may be reconverted to **1** by the removal of $MgBr_2$ as described by eq 5. The data thus show that **1** and **16** are

$$\underset{\mathbf{16}}{((THF)Mg)_6(NPh)_4Br_4} \xrightarrow[\text{4 equiv}]{\text{1,4-dioxane}} {}^{2}/_{3}\underset{\mathbf{1}}{((THF)MgNPh)_6} + 2MgBr_2\cdot 2(1,4\text{-dioxane}) \quad (5)$$

readily interconvertible by simple addition or removal of the appropriate number of equivalents of magnesium halide.

Conclusions

The reactions described here have shown **1** to be a capable imide transfer agent for the synthesis of a wide variety of main group imido compounds. While it was shown the reaction of **1** with ketone and nitroso compounds led to the formation of the corresponding imine and diimine products **4** and **5**, the synthetic utility of **1** as an imide transfer is perhaps best demonstrated in its reactions with main group 14 and 15 substrates. Formation of the diazadiphosphetidines **7** and **8** and the tetrameric group 14 imides **9**, **11**, and **12** is an indication of the potential of magnesium imides as versatile imide transfer agents especially in main group chemistry.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

Supporting Information Available: Full tables of data collection and refinement parameters, atom coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates and isotropic thermal parameters (54 pages). Ordering information is given on any current masthead page.

IC951510A

---

(30) For example: (a) Sinha, S. P.; Pakkann, T. T.; Pakkanen, T. A.; Niinisto, L. *Polyhedron* **1982**, 1, 355. (b) Tursina, A. I.; Yatsen, Ko, A. V.; Medvedev, S. V.; Aslanov, L. A. *Koord. Khim.* **1987**, *13*, 401.

(31) (a) Muller, N.; Lauterbur, P. C.; Goldenson, J. *J. Am. Chem. Soc.* **1956**, 478, 3557. (b) Van Wazer, J. R.; Callis, C. F.; Shoolery, J. N.; Jones, R. C. *J. Am. Chem. Soc.* **1956**, *78*, 5715.

(32) Reich, H. J.; Green, D. P. *J. Am. Chem. Soc.* **1989**, *111*, 8729.