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Synthesis, characterization and crystal structures of isothiocyanate and carbodiimide complexes derived from organomagnesium reagents: insertion into Mg–X (X = C or N) bonds

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A series of magnesium–isothiocyanate and –carbodiimide insertion products, $Mg(SCPhNBu^t)_2(thf)_2$ **1**, $Mg(SCPhNPh)_2(thf)_2$ **2**, $Mg(Pr^iNCRNPr^i)_2(thf)_2$ (R = Ph **3**, Et **4** or Pr^i **5**) and $Mg(Bu^tNCEtNBu^t)_2(thf)_2$ **6** have been prepared by the stoichiometric reaction between MgR_2 (R = Ph, Et or Pr^i) and various isothiocyanates and carbodiimides in tetrahydrofuran (thf) solution. The 1 : 1 reaction between bis(diisopropylamido)magnesium and 1,3-diisopropylcarbodiimide gave a dinuclear complex $Mg_2(\mu\text{-}NPr^i{}_2)_2[(Pr^iN)_2CNPr^i{}_2]_2$ **7** and a mononuclear complex $Mg[(Pr^iN)_2CNPr^i{}_2]_2(thf)$ **8** when the stoichiometry is 1 : 2. The mononuclear complexes $Mg[SC(NPh)NR_2]_2(thf)_2$ (R = Pr^i **9** or Et **10**) were obtained using phenyl isothiocyanate and bis(diethylamido)- or bis(diisopropylamido)-magnesium in 1 : 1 stoichiometric ratio. A plausible mechanism for the formation of **7** and **8** is suggested. Reaction between MgEtBr and PhNCS in diethyl ether gave the dinuclear complex $Mg_2(SCEtNPh)_4(OEt_2)_2$ **11**. All of the complexes were characterized by ^1H, ^{13}C NMR and IR spectroscopy as well as elemental analysis. The crystal structures of **1**, **3**, **8**, **9** and **11** were determined by single-crystal X-ray diffraction. The reaction of complex **1** with an excess of PhNCO resulted in the cyclotrimerization of phenyl isocyanate to give $(PhNCO)_3\cdot thf$.

The reaction between carbon dioxide and organometallic compounds is of interest because it provides a one-carbon homologization of the organic group.[1] A number of synthetic and mechanistic studies have been carried out on the insertion reactions of CO_2 into M−C, M−O, M−H and M−N bonds.[2] Recently we reported the CO_2-insertion reactions of polynuclear ethynyl-bridged aluminium–magnesium compounds which occur selectively at the metal–carbon rather than at the metal–nitrogen bond.[3] We attributed the high reactivity of the magnesium centre in comparison to that in Grignard reagents to its more electropositive nature. This interesting activity prompted us to investigate the reactivity of magnesium in dialkyl-, diaryl- and dialkylamido-magnesium compounds towards the isoelectronic analogues of CO_2 such as isothiocyanates and carbodiimides. While a few reactions of isothiocyanates with magnesium have been reported,[4] there are no structural data on insertions into the Mg−C bond. The insertion reactions of carbodiimides have also been studied extensively for transition metals[5] yet there is no report available on structurally characterized magnesium imidine compounds.

In this paper we report the synthesis and structural characterization of the products obtained from the insertion reaction of isothiocyanate and carbodiimide with diarylmagnesium compounds. The products are also coupled with migration of the aryl group onto the carbon of isothiocyanate or carbodiimide. The complexes obtained from the insertion reactions of the isothiocyanates are the first where the magnesium is bonded through both nitrogen and sulfur atoms. We also report on the complexes obtained from the reaction of dialkylamidomagnesium and various isothiocyanates and carbodiimides. The reaction of $Mg(SCPhNBu^t)_2(thf)_2$ **1** (thf = tetrahydrofuran) with phenyl isocyanate is also examined.

Results and Discussion

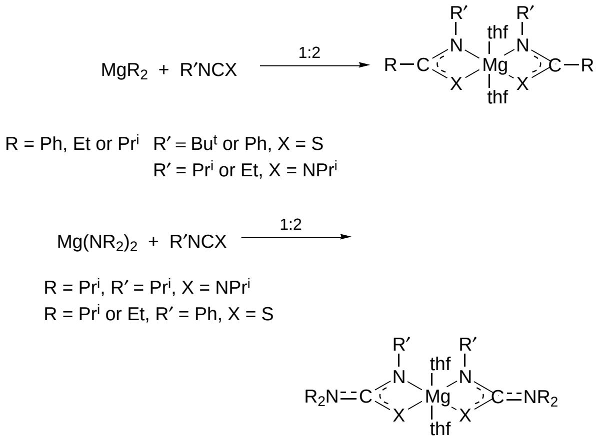
Synthesis and characterization

A 1 : 2 molar ratio of $MgPh_2$ to Bu^tNCS in tetrahydrofuran was allowed to react for 14–16 h at ambient temperature to yield $Mg(SCPhNBu^t)_2(thf)_2$ **1** in quantitative yield (Scheme 1). Similarly, $Mg(SCPhNPh)_2(thf)_2$ **2** was obtained using phenyl isothiocyanate. The reaction of diisopropylcarbodiimide and MgR_2 (R = Ph, Et or Pr^i), yielded the complexes $Mg(Pr^iNCRNPr^i)_2(thf)_2$ (R = Ph **3**, Et **4** or Pr^i **5**). The reaction of $Mg(NPr^i{}_2)_2$ with 1,3-diisopropylcarbodiimide in equimolar ratio gave the unsolvated dinuclear complex $Mg_2(\mu\text{-}NPr^i{}_2)_2[(Pr^iN)_2CNPr^i{}_2]_2$ **7**, while a similar reaction with 1 : 2 stoichiometry gave the mononuclear complex $Mg[(Pr^iN)_2CNPr^i{}_2]_2(thf)$ **8**. The reaction between $Mg(NR_2)_2$ (R = Pr^i or Et) and phenyl isothiocyanate in 1 : 2 stoichiometric ratio gave mononuclear complexes $Mg[SC(NPh)NR_2]_2(thf)_2$ (R = Pr^i **9** or Et **10**) (Scheme 1). The reaction between ethylmagnesium bromide, and phenyl isothiocyanate in 1 : 1 stoichiometric ratio in diethyl ether gave a dinuclear complex $Mg_2(SCEtNPh)_4(OEt_2)_2$ **11**. All of the complexes have been fully characterized by ^1H, ^{13}C NMR and IR spectroscopy and elemental analysis while some have been further characterized structurally by single-crystal X-ray diffraction.

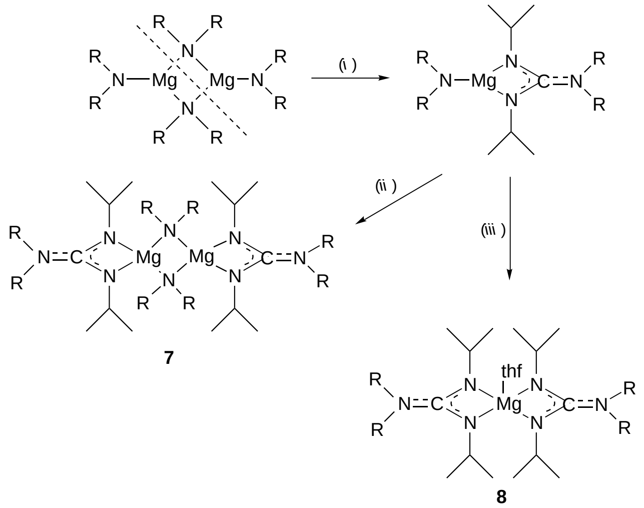
The IR spectra of the isothiocyanate complexes are consistent with the presence of isothiocyanate groups in the product. There is no band at *ca.* 2150 cm^{-1} attributable to an asymmetric N=C=S stretch and the bands observed are similar to those characteristic bands observed for MeC(S)NHMe (1550, 1200 and 720 cm^{-1}).[6] For the carbodiimide complexes the band at *ca.* 2100 cm^{-1} [ν_{asym}(N=C=N)] of the pure carbodiimide was absent and bands are present in the region 1500–1650 cm^{-1} assignable to C−N stretching and in the region 800–650 cm^{-1} attributable to metal–carbon stretches.

Spectroscopic studies

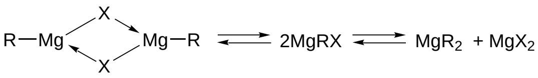
In the ^1H NMR spectrum of complex **1** a singlet was observed at δ 1.17 assigned to the methyl protons of the Bu^t group and a set of multiplets in the aromatic proton region assigned to the phenyl groups. Two singlets at δ 1.41 and 3.80 indicates the presence of co-ordinated thf. For complex **3** the signals at δ 1.21 and 3.37 are assigned as the isopropyl protons and the multi-



Scheme 1



Scheme 2 R = Pr^i. (*i*) RN=C=NR, 1 : 1; (*ii*) dimerization; (*iii*) excess of carbodiimide, thf



Scheme 3

$$2\,MgRX \longrightarrow MgR_2 + MgX_2$$
$$MgR_2 + PhNCS \longrightarrow \mathbf{11}$$

Scheme 4

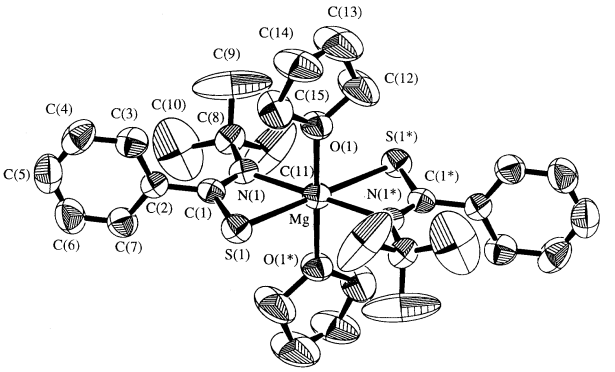


Fig. 1 An ORTEP[7] view of complex **1**. Thermal ellipsoids are drawn at the 50% probability level

plets in the region δ 6.88–7.25 to aromatic protons. For complex **7** the ^{1}H NMR spectrum is rather distinct with three sets of doublets and septets at δ 1.19, 1.27, 1.47 and at 3.39, 3.56, 3.87 respectively indicating the presence of three kinds of isopropyl groups (Scheme 2). These isopropyl groups have been identified as those attached to the nitrogen of the amido group, that of the group which arises from migration on to the carbon of the carbodiimide and those of the carbodiimide itself. For complex **8** the ^{1}H NMR spectrum indicates two sets of doublets and septets at δ 1.23, 1.32 and 3.48, 3.69 respectively besides two singlets assignable to the thf.

Monomeric complexes **9** and **10** (Scheme 1) showed only one set of doublet and septets at δ 1.25, 3.88 for **9** and at δ 1.11, 3.72 for **10** which were assigned to the isopropyl and ethyl groups attached to the carbon of phenyl isothiocyanate. Attempts to obtain structural data on **7** failed due to crystal decay during data collection.

In the ^{1}H NMR spectrum the dinuclear complex **11** gives two sets of signals for methylene groups (one due to CH_2 of ethyl at δ 2.49 and the second due to CH_2 of diethyl ether at δ 3.66) while the methyl protons have merged to give only one triplet at δ 1.06. The aromatic protons were observed in the region δ 6.8–7.5.

In an attempt to understand the mechanism of formation of the mono- and di-meric species, we have carried out independent experiments using MgR_2 and $Mg(NR_2)_2$ and isothiocyanates and carbodiimides. Typically, to a solution of organomagnesium reagents $MgPh_2$ and $Mg(NPr^i{}_2)_2$, diisopropylcarbodiimide was added either in equimolar ratio or in excess (1:1 and 1:2 stoichiometry). Interestingly, in the case of diarylmagnesium only a monomeric complex **3** was obtained while in the case of dialkylamidomagnesium both dimeric compound **7** and monomeric compound **8** have been obtained (Scheme 2). We attribute the formation of dimer **7** to the stability of $NPr^i{}_2$ acting as a bridging group in comparison to alkyl or aryl.

It is also interesting that the reaction between MgEtBr and phenyl isothiocyanate yielded a magnesium dimer, **11**, with sulfur as bridging group. In this case only the alkyl group showed preference to bromide in migrating to the carbon of isothiocyanate. It is well known that a Schlenk equilibrium (Scheme 3) exists for MgEtBr.

A mechanism for the formation of the dimeric species is given in Scheme 4. In this case MgR_2 reacts with phenyl isothiocyanate in 1:2 molar ratio to form the magnesium dimer, **11** with the sulfur atom of the chelated NCS unit bridging. The formation of a dimeric species (instead of a monomer similar to complex **1**) is attributed to steric factors. In the case of complex **1** two thf molecules occupy the apical sites on the magnesium atom which prevents formation of a dimer through sulfur bridges, while in the case of **11** only one diethyl ether group (less bulky) is co-ordinated to each of the magnesium atoms.

Structures of complexes 1, 3, 8, 9 and 11

$Mg(SCPhNBu^t)_2(thf)_2$ 1. Complex **1** was crystallized from thf solution. A perspective drawing of the structure is shown in Fig. 1. There is a puckering disorder of both axial thf molecules [C(12)–C(15) and C(12*)–C(15*)]. The Bu^t group exhibits higher thermal parameters than usual which may indicate minor rotational disorder [C(9)–C(11)]. The complex possesses an inversion centre and is best described as having a distorted octahedral geometry around the magnesium atom which is bonded through both sulfur and nitrogen atoms of the ligand. There are two molecules of thf at the apical positions. The four-membered ring Mg–S(1)–C(1)–N(1) is planar with a mean deviation of 0.02 Å. The S(1)–C(1) and C(1)–N(1) bond lengths, 1.744(6) and 1.297(7) Å respectively (Table 1), are between single- and double-bond values[8,9] (C–S 1.81 and 1.61, C–N 1.51 and 1.26 Å). This is consistent with the IR spectrum which shows no observable frequencies corresponding to C=N beyond 1550 cm^{-1}, which indicates delocalization of the NCS unit. The two thiobenzamide ligands are *trans* to each other, yet forming an almost coplanar framework. Steric factors are probably responsible for their orientation.

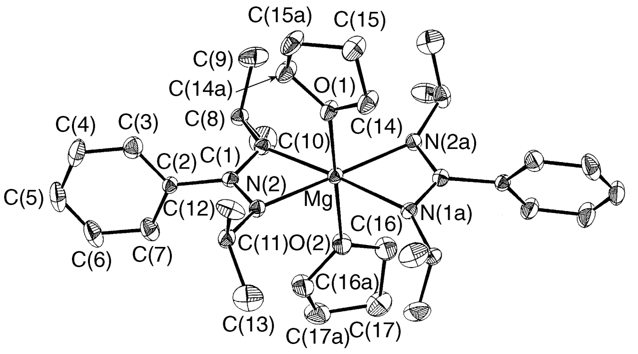


Fig. 2 An ORTEP view of complex **3**. Details as in Fig. 1

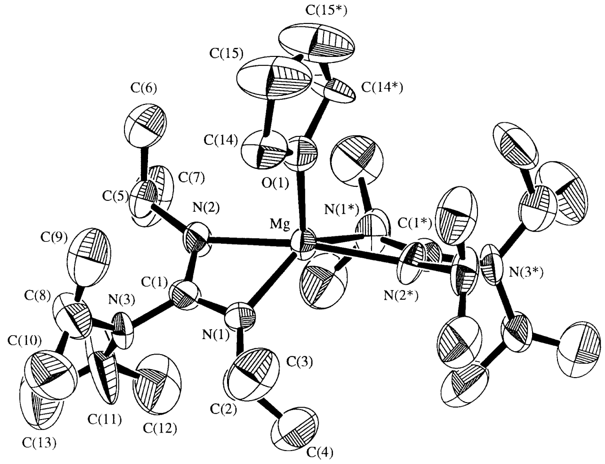


Fig. 3 An ORTEP view of compound **8**. Details as in Fig. 1

$Mg(Pr^iNCPhNPr^i)_2(thf)_2$ 3. The magnesium amidine complex **3** is structurally similar to **1**, and also possesses octahedral geometry around the magnesium. However, instead of an inversion centre, the molecule contains a two-fold axis passing through the O(1)–Mg–O(2) axis. The Mg–N distances of 2.168(6) and 2.161(6) Å in the chelated amidine groups are typical σ-bonding distances. The C–N bond lengths [1.325(10) and 1.338(10) Å] are intermediate between the typical C–N (1.47 Å) and C=N (1.27 Å) covalent distances, indicating delocalization over the NCN skeleton. Similar values were found for closely related platinum and palladium complexes (1.33 and 1.332 Å).[10,11] The NCN bite angle of 114.5(7)° is close to the corresponding value in $[Mo_2(PhNCPhNPh)_4]$ (117°).[12] An ORTEP view of the complex is given in Fig. 2.

$Mg[(Pr^iN)_2CNPr^i_2]_2(thf)$ 8. Complex **8** which was also crystallized from thf solution possesses a square-bipyramidal geometry around magnesium. The diisopropylcarbodiimide ligands act as bidentate chelates forming the basal plane and the solvent thf occupies the axial position. The structure contains a crystallographic two-fold axis passing through O(1) and Mg. An ORTEP view of the complex is given in Fig. 3. One isopropyl group on each of the carbodiimide ligands is disordered [C(11)–C(13) and two-fold related C(11*)–C(13*)]. The two disordered orientations are related by a mirror plane containing N(3), C(12) and C(13). The elongated ellipsoid of C(11) results from a combination of the two unresolved atomic positions of distorted C(11). The shorter distance between C(11) and N(3) as well as the planar arrangement around C(11) is also due to the disorder. A puckering disorder of thf [C(14), C(15), C(14*) and C(15*)] is also observed. Analogous to complex **3**, the Mg–N distances [2.066(7) and 2.183(6) Å] are typical of σ-bonding. These distances as well as Mg–O(1) [2.098(9) Å] are in good agreement with the values for porphyrin[13,14] or quadridentate Schiff-base derivatives.[15] The N(1)–C(1) and N(2)–C(1) bond lengths of 1.364(10) and 1.306(9) Å again indicate delocalization over the NCN skeleton. However the small but significant difference between these two bonds and the noticeable shortening of the Mg–N(1) bond when compared to Mg–N(2) seem to support a more localized model with more double-bond character of Mg–N(1) and almost single-bond character of Mg–N(2). The N(3)–C(1) distance of 1.431(9) Å is also longer than N(1)–C(1) and N(2)–C(1), consistent with a localized (or at least less delocalized) model. However, disorder of the attached isopropyl group has reduced the reliability of this assignment.

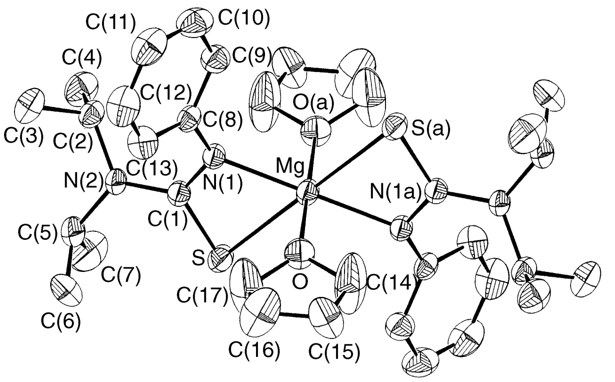


Fig. 4 An ORTEP view of complex **9**. Details as in Fig. 1

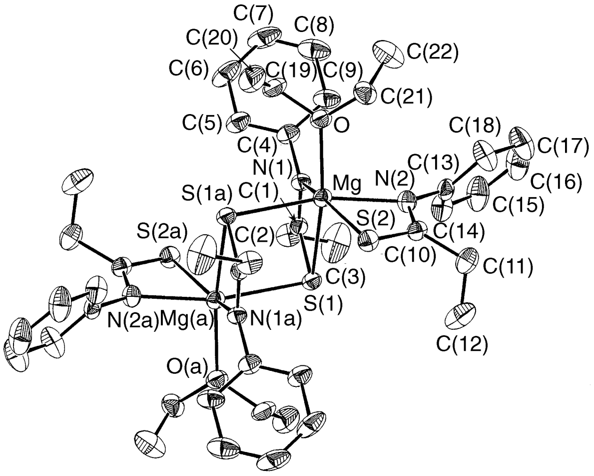
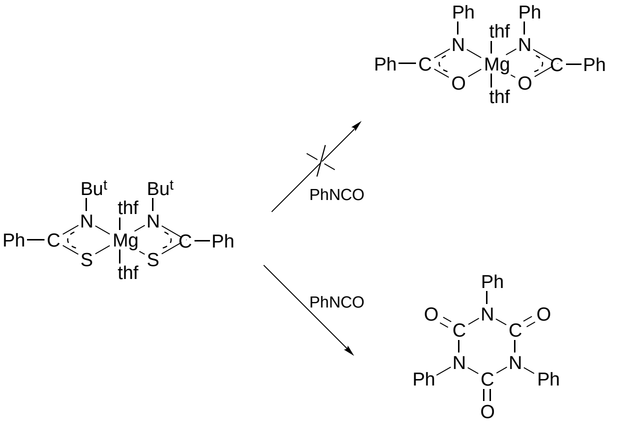


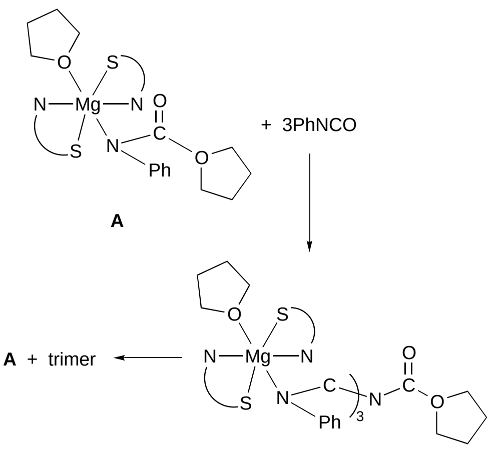
Fig. 5 An ORTEP view of complex **11**. Details as in Fig. 1

$Mg[SC(NPh)NPr^i_2]_2(thf)_2$ 9. The structure of complex **9** is monomeric. The thf molecules are disordered having two conformations with occupancies of 50% each [C(14)–C(17), 50%; C(14′)–C(17′), 50%]. Only the C(14)–C(17) conformation is shown in the ORTEP plot (Fig. 4). The geometry of the magnesium centre is best described as axially compressed rhombic. The observed *trans* ligation of the two ligand moieties with Mg–S and Mg–N distances of 2.5595(13) and 2.1117(23) Å respectively is responsible for this geometry. The axial coordination sites are occupied by the oxygen atoms of two thf molecules. By virtue of the presence of an inversion centre at magnesium, the molecule possesses two-fold symmetry. The equatorial donor atoms form a rhombic plane in which the magnesium atom also lies. The Mg–O bonds are nearly perpendicular to this plane with N–Mg–O and S–Mg–O bond angles of 90.14(9) and 91.13(8)° respectively. The observed C(1)–S and C(1)–N(1) distances of 1.736(3) and 1.324(4) are consistent with C–S and C–N bonds, clearly establishing the identity of the ligand unit.

$Mg_2(SCEtNPh)_4(OEt_2)_2$ 11. The structure of the complex **11** consists of discrete dimeric molecules (Fig. 5). The two magnesium centres are symmetrically related to each other due to



Scheme 5



Scheme 6

the presence of a centre of inversion between them. The bidentate PhNCS ligand binds the metal in two different modes. In one the sulfur and nitrogen atoms occupy equatorial positions, and in the second they occupy equatorial and axial positions respectively. The axial sulfur atom is also shared by the other symmetrically related magnesium, to which the sulfur atom is an equatorial donor. The remaining axial position is occupied by the oxygen atom of a solvent diethyl ether molecule. The geometry of the six-co-ordinate magnesium is distorted octahedral. The Mg–S bonds are considerably longer than the Mg–N and the axial and equatorial Mg–S distances are unequal as could be expected (see Table 1). Unlike in complex **9**, the four equatorial and the central magnesium atoms are not planar; the axial Mg–O and Mg–S bonds also deviate from perpendicular to the least-squares plane. The Mg–S(1) distance of the bridging sulfur, 2.690(3) Å, is considerably longer (nearly 0.16 Å) than the Mg–S(2) distance of the chelated NCS unit. The NCS units chelate to the magnesium with N(1)–Mg–S(1) and N(2)–Mg–S(2) angles of 63.61(17) and 65.65(17)° respectively. The S(1)–C(1) and C(1)–N(1) bond lengths, 1.768(7) and 1.288(10) Å, are in the range between single- and double-bond values with the C–N bond having more double-bond character than the C–S bond.

The dimeric structure of this complex seems to be the result of the two modes of co-ordination exhibited by the ligand, which also preclude the formation of any polymeric species. A comparison of the structural features of **9** and **11** suggests that a similar dimeric structure for the former complex will be sterically disfavoured due to the presence of the bulky diisopropylamido substitution at the carbon atom.

Reaction of complex 1 with an excess of isocyanate

The reaction of complex **1** with an excess of phenyl isocyanate was carried out in an attempt to examine the possibility of ligand replacement (Scheme 5). Surprisingly, the isocyanate ligand trimerizes in the presence of **1** and crystallizes out as the cyanurate in the form of a thf adduct in quantitative yield. Even though the formation of this trimer has been well documented, the nature of the catalyst is quite different. Earlier reports suggest that the conversion of isocyanates into cyanurates uses catalytic amounts of $AlCl_3$–NaCl[16] or $SnR_3(OR')$.[17] Similar cyclotrimerization reactions have been reported using phenyl isocyanate and dihydrosilanes.[18] The trimerization of aryl isocyanates can be explained by repeated insertion of PhNCO into the Mg–O (thf) bond of complex **1**. After three insertions, elimination of trimer with reformation of the intermediate magnesium amide occurs (Scheme 6).

Conclusion

We have demonstrated that a variety of insertion products can be prepared using various organomagnesium reagents and isothiocyanates and carbodiimides. The reaction between MgR_2 and isothiocyanates/carbodiimides is independent of stoichiometry, while analogous reactions of $Mg(NR_2)_2$ with isothiocyanates/carbodiimides are solely dependent on the stoichiometry. This has been attributed to the probable preference of dialkylamide to act as bridging group to give dimers rather than dialkyl- or diaryl-magnesium compounds. Complex **1** acts as a good catalyst for the cyclotrimerization of isocyanates.

Experimental

All experiments were carried out in a N_2-flushed glove-bag, dry-box or *in vacuo* using standard Schlenk techniques.[19] All solvents were distilled and degassed prior to use. Phenyl isocyanate, phenyl isothiocyanate, *tert*-butyl isothiocyanate, 1,3-diisopropylcarbodiimide and di-*tert*-butylcarbodiimide were obtained from Aldrich and used as received. All ^1H and ^{13}C NMR spectra were recorded on a Varian VXR-300 spectrometer, chemical shifts being referred to either $SiMe_4$ (^1H) or C_6D_6 (^1H, δ 7.15; ^{13}C-{^1H}, δ 128.00), IR spectra as Nujol mulls between KBr discs on a Bio-Rad FTS-40 FT-IR spectrometer. Elemental analyses (C, H and N) were performed at the Analytische Laboratorien of H. Malissa und G. Reuter GmbH, Germany. Deviations in the results from calculated values are attributed to the extremely air-sensitive and hygroscopic nature of these compounds. The starting materials MgR_2 (R = Ph, Et or Pr^i) and $Mg(NR_2)_2$ (R = Pr^i or Et) were prepared according to literature methods.[20]

Syntheses

$Mg(SCPhNBu^t)_2(thf)_2$ 1. Complexes **1**–**6** were prepared by using a general procedure involving MgR_2 (R = Ph, Et or Pr^i) and various isothiocyanates and carbodiimides. In a typical procedure for **1**, a solution of $MgPh_2$ (1.78 g, 10 mmol) in tetrahydrofuran (40 cm^3) was added to a solution of Bu^tNCS (1.06 g, 10 mmol) in thf (10 cm^3). The resulting solution was stirred for 14–16 h at ambient temperature, then reduced in volume to *ca.* 25 cm^3. Keeping the saturated solution at room temperature for 2 d resulted in a 70% yield of colourless crystals of **1**, m.p. 230 °C (decomp.). NMR (C_6D_6, 297 K, 300 MHz): ^1H, δ 1.17 [s, 8 H, $C(CH_3)_3$], 1.41 (s, 8 H, $C^{3,4}H_2$ of thf), 3.80 (s, 8 H, $C^{2,5}H_2$ of thf), 7.04 (m, 2 *p*-H, C_6H_5), 7.28 (m, 4 *m*-H, C_6H_5) and 7.31 (m, 4 *o*-H, C_6H_5); ^{13}C, δ 25.47 ($C^{3,4}$ of thf), 31.83 [$C(CH_3)_3$], 57.71 [$C(CH_3)_3$], 68.39 ($C^{2,5}$ of thf), 125.68 (*p*-C, C_6H_5), 126.96 (*m*-C, C_6H_5), 128.30 (*o*-C, C_6H_5) and 192.25 (NCS). IR (Nujol, cm^{-1}): 2910w, 2725w, 1541s, 1470s, 1390s, 1216s, 1038s, 927s, 791s and 723s (Found: C, 65.1; H, 8.1; N, 4.95. Calc. for $C_{22}H_{28}MgN_2S_2$·2thf: C, 65.15; H, 8.0; N, 5.05%).

$Mg(SCPhNPh)_2(thf)_2$ 2. M.p. 210–212 °C (decomp.). NMR (C_6D_6, 297 K, 300 MHz): ^1H, δ 1.32 (s, 8 H, $C^{3,4}H_2$ of thf), 3.72 (s, 8 H, $C^{2,5}H_2$ of thf), 6.90 (m, 4 *p*-H, C_6H_5), 6.96 (m, 8 *m*-H,

Table 1 Selected bond distances (Å) and angles (°) for complexes **1**, **3**, **8**, **9** and **11**

$Mg(SCPhNBu^t)_2(thf)_2$ **1**

Mg–N(1)	2.176(5)	N(1)–C(1)	1.297(7)
Mg–S(1)	2.584(2)	N(1)–C(8)	1.495(7)
Mg–O(1)	2.230(4)	C(1)–C(2)	1.484(8)
C(1)–S(1)	1.744(6)		

Mg–N(1)–C(1)	101.0(4)	Mg–N(1)–C(8)	133.1(4)
Mg–S(1)–C(1)	75.7(2)	C(1)–N(1)–C(8)	125.8(5)
N(1)–C(1)–S(1)	117.4(5)	N(1)–Mg–O(1)	90.8(2)
Mg–O(1)–C(12)	123.0(4)	S(1)–C(1)–C(2)	114.9(4)

$Mg(Pr^iNCPhNPr^i)_2(thf)_2$ **3**

Mg–N(1)	2.168(6)	N(1)–C(1)	1.325(10)
Mg–N(2)	2.161(6)	N(1)–C(8)	1.464(9)
Mg–O(1)	2.226(9)	N(2)–C(1)	1.338(10)
Mg–O(2)	2.331(9)	N(2)–C(11)	1.457(10)
O(1)–C(14)	1.410(10)	C(1)–N(2)	1.338(10)
O(2)–C(16)	1.404(11)	C(1)–C(2)	1.500(10)

O(1)–Mg–O(2)	180.0	N(2)–Mg–N(2)	179.2(3)
O(1)–Mg–N(1)	92.8(2)	Mg–O(1)–C(14)	124.8(5)
O(1)–Mg–N(2)	89.6(2)	Mg–N(1)–C(1)	91.6(4)
O(2)–Mg–N(1)	87.2(2)	Mg–N(1)–C(8)	146.7(5)
O(2)–Mg–N(2)	90.4(2)	Mg–N(2)–C(1)	91.5(4)
N(1)–Mg–N(1)	174.4(3)	N(1)–C(1)–N(2)	114.5(7)
N(1)–Mg–N(2)	62.3(2)	N(1)–C(1)–C(2)	122.3(7)

$Mg[(Pr^iN)_2CNPr^i_2]_2(thf)$ **8**

Mg–O(1)	2.098(9)	N(2)–C(1)	1.306(9)
Mg–N(1)	2.066(7)	N(2)–C(5)	1.478(9)
Mg–N(2)	2.183(6)	N(3)–C(1)	1.431(9)
Mg–C(1)	2.550(9)	N(3)–C(8)	1.44(1)
O(1)–C(14)	1.478(8)	N(3)–C(11)	1.42(1)
N(1)–C(1)	1.364(10)	C(2)–C(3)	1.51(1)
N(1)–C(2)	1.431(10)		

O(1)–Mg–N(1)	111.9(2)	C(1)–Mg–C(1*)	146.5(4)
O(1)–Mg–N(2)	94.7(2)	Mg–O(1)–C(14)	123.0(5)
O(1)–Mg–C(1)	106.8(2)	C(1)–N(1)–C(2)	121.7(7)
N(1)–Mg–N(1*)	136.2(4)	Mg–N(2)–C(1)	90.3(5)
N(1)–Mg–N(2)	63.0(2)	Mg–N(2)–C(5)	147.0(6)
N(1)–Mg–N(2*)	113.1(3)	C(1)–N(3)–C(8)	119.8(8)
N(1)–Mg–C(1)	32.3(3)	Mg–C(1)–N(3)	173.7(6)
N(1)–Mg–C(1*)	129.1(3)	Mg–C(1)–N(2)	58.9(4)
N(2)–Mg–N(2*)	170.6(4)	N(1)–C(1)–N(2)	112.6(8)
N(2)–Mg–C(1)	30.8(2)	N(1)–C(1)–N(3)	121.4(8)
N(2)–Mg–C(1*)	144.2(3)	N(2)–C(1)–N(3)	126.0(8)

$Mg[SC(NPh)NPr^i_2]_2(thf)_2$ **9**

Mg–S	2.5595(13)	N(2)–C(1)	1.370(4)
Mg–O	2.191(2)	N(1)–C(8)	1.413(4)
Mg–N(1)	2.112(2)	N(2)–C(2)	1.479(4)
S–C(1)	1.736(3)	N(2)–C(5)	1.483(4)
N(1)–C(1)	1.324(4)		

S–Mg–S(a)	180.0	Mg–N(1)–C(1)	102.3(2)
S–Mg–O	91.13(8)	Mg–N(1)–C(8)	130.2(2)
S–Mg–N(1)	66.40(8)	C(1)–N(1)–C(8)	124.8(2)
S–Mg–N(1a)	113.60(8)	C(1)–N(2)–C(2)	119.9(2)
O–Mg–N(1)	90.14(9)	S–C(1)–N(1)	114.7(2)
N(1)–Mg–N(1a)	180.0	S–C(1)–N(2)	121.0(2)
Mg–S–C(1)	75.93(11)	N(1)–C(1)–N(2)	124.3(3)
Mg–O–C(14)	127.9(5)		

$Mg_2(SCEtNPh)_4(OEt_2)_2$ **11**

Mg–S(1)	2.690(3)	S(1)–C(1)	1.768(7)
Mg–S(1a)	2.657(3)	S(2)–C(10)	1.699(8)
Mg–S(2)	2.535(3)	O–C(19)	1.449(9)
Mg–O	2.099(6)	N(1)–C(1)	1.288(10)
Mg–N(1)	2.138(6)	N(1)–C(4)	1.450(9)
Mg–N(2)	2.185(6)	N(2)–C(10)	1.309(9)
Mg–C(10)	2.715(7)	N(2)–C(13)	1.442(9)
S(1)–Mg(a)	2.657(3)	C(1)–C(2)	1.487(11)

S(1)–Mg–S(1a)	85.61(10)	N(2)–Mg–C(10)	28.5(2)
S(1)–Mg–S(2)	99.64(10)	Mg–S(1)–Mg(a)	94.39(10)
S(1)–Mg–O	157.8(2)	Mg–S(1)–C(1)	74.6(3)
S(1)–Mg–N(1)	63.6(2)	Mg(a)–S(1)–C(1)	97.2(3)
S(1)–Mg–N(2)	91.1(2)	Mg–S(2)–C(10)	77.0(3)
S(1)–Mg–C(10)	92.1(2)	Mg–O–C(19)	122.7(5)
S(1a)–Mg–S(2)	98.14(10)	Mg–N(1)–C(1)	107.0(4)
S(1a)–Mg–O	94.7(2)	Mg–N(1)–C(4)	131.8(5)
S(1a)–Mg–N(1)	93.0(2)	C(1)–N(1)–C(4)	121.2(6)
S(1a)–Mg–N(2)	162.7(2)	Mg–N(2)–C(10)	98.8(5)
S(1a)–Mg–C(10)	134.6(2)	Mg–N(2)–C(13)	138.6(5)
S(2)–Mg–O	102.3(2)	C(10)–N(2)–C(13)	121.4(6)
S(2)–Mg–N(1)	159.2(2)	S(1)–C(1)–N(1)	114.8(5)
S(2)–Mg–N(2)	65.7(2)	S(1)–C(1)–C(2)	118.8(6)
S(2)–Mg–C(10)	37.6(2)	N(1)–C(1)–C(2)	126.4(6)
O–Mg–N(1)	94.2(2)	Mg–C(10)–S(2)	65.5(2)
O–Mg–C(10)	103.1(2)	Mg–C(10)–N(2)	52.7(4)
N(1)–Mg–N(2)	100.8(2)	S(2)–C(10)–N(2)	117.2(5)
N(1)–Mg–C(10)	126.2(3)	N(2)–C(10)–C(11)	123.5(7)

C_6H_5) and 7.62 (m, 8 *o*-H, C_6H_5); ^{13}C, δ 25.41 ($C^{3,4}$ of thf), 68.77 ($C^{2,5}$ of thf), 123.38 (*p*-C, C_6H_5), 124.42 (*m*-C, C_6H_5), 128.98 (*o*-C, C_6H_5) and 196.28 (NCS). IR (Nujol, cm^{-1}): 2922w, 2715w, 1521s, 1462s, 1368s, 1186s, 1043s, 922s, 795s and 713s (Found: C, 68.6; H, 6.1; N, 4.55. Calc. for $C_{26}H_{20}MgN_2S_2\cdot 2thf$: C, 68.85; H, 6.15; N, 4.7%).

$Mg(Pr^iNCPhNPr^i)_2(thf)_2$ 3. M.p. 64–66 °C. NMR (C_6D_6, 297 K, 300 MHz): ^1H, δ 1.21 [d, 24 H, $NCH(CH_3)_2$], 1.40 (s, 8 H, $C^{3,4}H_2$ of thf), 3.37 [spt, 4 H, $NCH(CH_3)_2$], 3.80 (s, 8 H, $C^{2,5}H_2$ of thf) and 7.25 (m, 10 H, C_6H_5); ^{13}C, δ 25.24 ($C^{3,4}$ of thf), 26.70 [$NCH(CH_3)_2$], 47.10 [$NCH(CH_3)_2$], 68.56 ($C^{2,5}$ of thf) and 127.26 (C_6H_5). IR (Nujol, cm^{-1}): 2935s, 1627m, 1470s, 1382m, 1168w, 1143w, 1082w and 1022w (Found: C, 69.45; H, 9.65; N, 10.1. Calc. for $C_{26}H_{38}MgN_4\cdot 2thf$: C, 69.75; H, 9.8; N, 10.15%).

$Mg(Pr^iNCEtNPr^i)_2(thf)_2$ 4. M.p. 290 °C (decomp.). NMR (C_6D_6, 297 K, 300 MHz): ^1H, δ 1.01 [t, 6 H, $C(CH_2CH_3)$], 1.14 [d, 24 H, $NCH(CH_3)_2$], 2.13 [q, 4 H, $C(CH_2CH_3)$], 1.45 (s, 8 H, $C^{3,4}H_2$ of thf), 3.50 [spt, 4 H, $NCH(CH_3)_2$] and 3.80 (s, 8 H, $C^{2,5}H_2$ of thf); ^{13}C, δ 12.89 [$C(CH_2CH_3)$], 19.03 [$C(CH_2CH_3)$], 25.68 ($C^{3,4}$ of thf), 26.83 [$NCH(CH_3)_2$], 45.41 [$NCH(CH_3)_2$] and 67.86 ($C^{2,5}$ of thf). IR (Nujol, cm^{-1}): 2961s, 1628m, 1489s, 1372s, 1342s, 1242s and 1079m (Found: C, 64.35; H, 11.45; N, 16.2. Calc. for $C_{18}H_{38}MgN_4$: C, 64.65; H, 11.4; N, 16.75%).

$Mg(Pr^iNCPr^iNPr^i)_2(thf)_2$ 5. M.p. 210–212 °C. NMR (C_6D_6, 297 K, 300 MHz): ^1H, δ 1.12 [d, 24 H, $NCH(CH_3)_2$], 1.18 [d, 12 H, $CCH(CH_3)_2$], 1.38 (s, 8 H, $C^{3,4}H_2$ of thf), 3.00 [spt, 2 H, $CCH(CH_3)_2$], 3.66 [spt, 4 H, $NCH(CH_3)_2$] and 3.82 (s, 8 H, $C^{2,5}H_2$ of thf); ^{13}C, δ 20.05 [$CCH(CH_3)_2$], 24.24 ($C^{3,4}$ of thf), 27.15 [$CCH(CH_3)_2$], 27.58 [$NCH(CH_3)_2$], 45.05 [$NCH(CH_3)_2$], 68.42 ($C^{2,5}$ of thf) and 179.27 (NCN). IR (Nujol, cm^{-1}): 2968s, 1649m, 1486s, 1382s, 1312s, 1239s, 1108m and 1047m (Found: C, 66.2; H, 11.65; N, 15.25. Calc. for $C_{20}H_{42}MgN_4\cdot 2thf$: C, 66.3; H, 11.6; N, 15.45%).

$Mg(Bu^tNCEtNBu^t)_2(thf)_2$ 6. M.p. 195–197 °C. NMR (C_6D_6, 297 K, 300 MHz): ^1H, δ 1.19 [t, 6 H, $C(CH_2CH_3)$], 1.30 [s, 36 H, $NC(CH_3)_3$], 1.42 (s, 8 H, $C^{3,4}H_2$ of thf), 2.41 [q, 4 H, $C(CH_2CH_3)$] and 3.70 (s, 8 H, $C^{2,5}H_2$ of thf); ^{13}C, δ 15.05 [$C(CH_2CH_3)$], 20.67 ($C^{3,4}$ of thf), 23.34 [$C(CH_2CH_3)$], 33.64 [$NC(CH_3)_3$], 50.52 [$NC(CH_3)_3$], 65.32 ($C^{2,5}$ of thf) and 179.68 (NCN). IR (Nujol, cm^{-1}): 2904s, 1658w, 1469s and 1386s (Found: C, 62.55; H, 10.25; N, 13.1. Calc. for $C_{22}H_{46}MgN_4$: C, 62.85; H, 10.45; N, 13.35%).

$Mg_2(\mu\text{-}NPr^i_2)_2[(Pr^iN)_2CNPr^i_2]_2$ 7 and $Mg[(Pr^iN)_2CNPr^i_2]_2(thf)$ 8. To a thf solution (40 cm^3) of $Mg(NPr^i_2)_2$ (2.24 g, 10 mmol) was added 1,3-diisopropylcarbodiimide in equimolar quantity (1.26 g, 10 mmol for complex **7**) and in 1:2 ratio (2.52 g, 20

Table 2 Crystal and intensity collection data for complexes **1**, **3**, **8**, **9** and **11**[a]

	1	**3**	**8**	**9**	**11**
Formula	$C_{15}H_{22}MgNOS$	$C_{34}H_{54}MgN_4O_2$	$C_{30}H_{64}MgN_6O$	$C_{34}H_{54}MgN_4O_2S_2$	$C_{44}H_{60}Mg_2N_4O_2S_4$
M	288.71	575.13	549.18	639.24	853.83
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$C2/c$	$C2/c$ (no. 15)	$P\bar{1}$	$P2_1/n$
a/Å	8.887(3)	15.523(5)	20.669(4)	7.840(4)	12.210(3)
b/Å	9.373(3)	12.695(4)	10.615(4)	9.300(4)	10.815(4)
c/Å	10.573(4)	18.306(3)	16.910(4)	13.247(5)	18.505(6)
α/°	72.21(3)	—	—	79.03(3)	—
β/°	86.89(3)	103.12	98.47(2)	77.59(3)	98.07(3)
γ/°	68.28(2)	—	—	86.69(3)	—
U/Å^3	777.4(5)	3513.4(17)	3669(1)	926.0(7)	2419.4(13)
Z	2	4	4	1	2
F(000)	310.0	1257.0	1224.0	346	913
D_c/g cm^{-3}	1.233	1.087	0.994	1.146	1.172
μ/cm^{-1}	2.41	1.218	0.76	1.936	2.490
$2\theta_{max}$/°	47.1	45.0	47.1	45.0	45.0
Crystal dimensions/mm	0.33 × 0.42 × 0.45	0.50 × 0.50 × 0.50	0.46 × 0.50 × 0.61	0.40 × 0.40 × 0.50	0.50 × 0.60 × 0.60
No. measured reflections	2478	2314	2991	2425	3150
No. unique reflections	2312	2294	2900	2412	3150
No. observed reflections	1455 [$I > 3.0\sigma(I)$]	1539 [$I > 2.0\sigma(I)$]	1025 [$I > 3.0\sigma(I)$]	1724 [$I > 2.0\sigma(I)$]	1676 [$I > 2.0\sigma(I)$]
No. variables	169	188	173	233	253
R, R'	0.070, 0.083	0.083, 0.108	0.078, 0.050	0.040, 0.041	0.057, 0.063
Data collection temperature/°C	23	25	23	25	25
Goodness of fit	3.80	2.86	3.39	2.06	1.68
Intensity decay (%)	33.8	50	0	6	10

[a] Weighting scheme $w = [\sigma^2(F_o) + p^2/4F_o^{\,2}]^{-1}$; $p = 0.02$ for **1** and 0.002 for **8**; unit weights used for **3** and **11**; $w = 1/[\sigma^2(F_o)]$ for **9**.

mmol for **8**) in thf (10 cm^3) and the mixture was stirred for 12 h. The solution was centrifuged to remove insoluble material and upon cooling deposited colourless crystals. These turned to a white powder upon complete removal of solvent. Yield 70%.

Complex **7**: m.p. 120 °C (decomp.). NMR (C_6D_6, 297 K, 300 MHz): ^{1}H, δ 1.19 {d, 24 H, $CN[CH(CH_3)_2]_2$}, 1.27 [d, 24 H, $MgNCH(CH_3)_2$], 1.47 {d, $Mg_2N[CH(CH_3)_2]$}, 3.39 {spt, 4 H, $CN[CH(CH_3)_2]_2$}, 3.56 [spt, 4 H, $MgNCH(CH_3)_2$] and 3.87 {spt, $Mg_2N[CH(CH_3)_2]_2$}; ^{13}C, δ 22.94 {$CN[CH(CH_3)_2]_2$}, 26.31 [$MgNCH(CH_3)_2$], 27.76 {$Mg_2N[CH(CH_3)_2]$}, 45.97 {$CN[CH(CH_3)_2]_2$}, 46.75 [$MgNCH(CH_3)_2$], 48.01 {$Mg_2N[CH(CH_3)_2]$} and 170.49 (NCN). IR (Nujol, cm^{-1}): 2967s, 1640m, 1454s, 1384s, 1241s, 1161s and 989m (Found: C, 64.8; H, 11.95; N, 15.85. Calc. for $C_{38}H_{84}Mg_2N_8$: C, 65.1; H, 12.0; N, 16.0%).

Complex **8**: m.p. 144 °C. NMR (C_6D_6, 297 K, 300 MHz): ^{1}H, δ 1.23 {d, 24 H, $N[CH(CH_3)_2]_2$}, 1.32 [d, 24 H, $CH(CH_3)_2$], 1.41 (s, 4 H, $C^{3,4}H_2$ of thf), 3.48 {spt, 4 H, $N[CH(CH_3)_2]_2$}, 3.59 (s, 4 H, $C^{2,5}$ of thf) and 3.69 [spt, 4 H, $CH(CH_3)_2$]; ^{13}C, δ 22.10 {$N[CH(CH_3)_2]_2$}, 23.60 [$CH(CH_3)_2$], 25.44 ($C^{3,4}$ of thf), 46.02 {$N[CH(CH_3)_2]_2$}, 47.21 [$CH(CH_3)_2$] and 67.79 ($C^{2,5}$ of thf). IR (Nujol, cm^{-1}): 2960s, 1640s, 1442s, 1380s, 1225s, 1148s and 978m (Found: C, 64.8; H, 12.1; N, 17.4. Calc. for $C_{26}H_{56}MgN_6$: C, 65.58; H, 11.75; N, 17.65%).

$Mg[SC(NPh)NR_2]_2(thf)_2$ (R = Pr^i 9 or Et 10). Phenyl isothiocyanate (2.70 g, 20 mmol) in thf (20 cm^3) was added to $Mg(NR_2)_2$ (2.26 g, 10 mmol for **9** and 1.68 g, 10 mmol for **10**) in thf (80 cm^3) through an addition funnel in 2 : 1 stoichiometric ratio. The resulting pale yellow solution was allowed to stir overnight and the crude product was recrystallized from thf to yield white solid compounds **9** and **10**. Complex **9**: NMR (C_6D_6, 297 K, 300 MHz): ^{1}H, δ 1.25 [d, 24 H, $CH(CH_3)_2$], 1.34 (s, 8 H, $C^{3,4}H_2$ of thf), 3.70 (s, 8 H, $C^{2,5}H_2$ of thf), 3.88 [spt, 4 H, $CH(CH_3)_2$], 6.84 (m, 2 *p*-H, C_6H_5), 7.11 (m, 4 *m*-H, C_6H_5) and 7.30 (m, 4 *o*-H, C_6H_5); ^{13}C, δ 22.82 [$CNCH(CH_3)_2$], 24.42 ($C^{3,4}$ of thf), 45.64 [$CNCH(CH_3)_2$], 66.54 ($C^{2,5}$ of thf), 122.25 (*p*-C of C_6H_5), 126.43 (*m*-C of C_6H_5), 132.42 (*o*-C of C_6H_5) and 190.20 (NCS). IR (Nujol, cm^{-1}): 2951w, 2720w, 1531s, 1460s, 1390s, 1216s, 1036s, 926s, 792s and 720s (Found: C, 64.1; H, 8.7; N, 8.45. Calc. for $C_{26}H_{38}MgN_4S_2$: C, 63.95; H, 8.45; N, 8.75%).

Complex **10**: NMR (C_6D_6, 297 K, 300 MHz): ^{1}H, δ 1.11 [t, 12 H, $N(CH_2CH_3)_2$], 1.34 (s, 8 H, $C^{3,4}H_2$ of thf), 3.54 (s, 8 H, $C^{2,5}H_2$ of thf), 3.72 [spt, 8 H, $N(CH_2CH_3)_2$], 6.92 (m, 2 *p*-H, C_6H_5), 7.04 (m, 4 *m*-H, C_6H_5) and 7.27 (m, 4 *o*-H, C_6H_5); ^{13}C, δ 12.54 [$N(CH_2CH_3)_2$], 22.45 ($C^{3,4}$ of thf), 45.21 [$N(CH_2CH_3)_2$], 65.42 ($C^{2,5}$ of thf) and 198.2 (NCS). IR (Nujol, cm^{-1}): 2940w, 2711w, 1543s, 1470s, 1392s, 1210s, 1040s, 920s, 794s and 714s (Found: C, 61.4; H, 8.0; N, 9.95. Calc. for $C_{22}H_{30}MgN_4S_2$: C, 61.85; H, 7.9; N, 9.6%).

$Mg_2(SCEtNPh)_4(OEt_2)_2$ 11. To a solution of MgEtBr (1.33 g, 10 mmol) in diethyl ether (80 cm^3) was added dropwise a solution of phenyl isothiocyanate (1.35 g, 10 mmol) in diethyl ether (20 cm^3). The reaction took place immediately and a pale yellow solution was obtained. The reaction was allowed to continue overnight and the solution was centrifuged. Colourless crystals of complex **11** were obtained upon cooling. Yield 75%, m.p. 205–206 °C. NMR (C_6D_6, 297 K, 300 MHz): ^{1}H, δ 1.06 [t, 24 H, CH_2CH_3, $O(CH_2CH_3)_2$], 2.49 [t, 8 H, $O(CH_2CH_3)_2$], 3.33 (t, 8 H, CH_2CH_3), 6.87 (m, 4 *p*-H, C_6H_5), 7.01 (m, 8 *m*-H, C_6H_5) and 7.04 (m, 4 *o*-H, C_6H_5); ^{13}C, δ 13.27 [$O(CH_2CH_3)_2$], 15.26 (CH_2CH_3), 32.98 [$O(CH_2CH_3)_2$], 65.73 (CH_2CH_3), 123.35 (*p*-C of C_6H_5), 124.82 (*o*-C of C_6H_5) and 129.03 (*m*-C of C_6H_5). IR (Nujol, cm^{-1}): 2970w, 1541s, 1493s, 1367s, 1215s, 1070s, 914s, 783s and 713s (Found: C, 61.5; H, 6.85; N, 6.4. Calc. for $C_{36}H_{40}Mg_2N_4S_4\cdot 2OEt_2$: C, 61.75; H, 7.05; N, 6.55%).

$(PhNCO)_3\cdot thf$. To a thf solution (50 cm^3) of complex **1** (0.52 g, 1 mmol) was added phenyl isocyanate (0.364 g, 3 mmol) and the mixture was stirred for 12 h. A colourless crystalline solid was deposited upon slow cooling. M.p. 210 °C. NMR (C_6D_6, 297 K, 300 MHz): ^{1}H, δ 1.43 (s, 8 H, $C^{3,4}H_2$ of thf), 3.56 (s, 8 H, $C^{2,5}H_2$ of thf), 7.12 (m, 4 *p*-H, C_6H_5), 7.20 (m, 8 *m*-H) and 7.28 (m, 8 *o*-H, C_6H_5); ^{13}C, δ 25.77 ($C^{3,4}$ of thf), 67.83 ($C^{2,5}$ of thf), 121.28 (*p*-C of C_6H_5), 129.62 (*o*-C of C_6H_5), 131.75 (*m*-C of C_6H_5) and 167.66 (NCO). IR (Nujol, cm^{-1}): 2922w, 1710s, 1490s, 1462s, 1378s, 1073s and 753s (Found: C, 69.45; H, 4.2; N, 11.55. Calc. for $C_{21}H_{15}N_3O_3$: C, 70.6; H, 4.2; N, 11.75%). A preliminary X-ray structural analysis confirmed the identity of the compound. However, its poor quality prevents publication. Further attempts to improve the data failed. An ORTEP drawing is available as supplementary material.

Crystallography

Suitable single crystals of complexes **1**, **3**, **8**, **9** and **11** were sealed in glass capillaries. Preliminary examination and intensity-data collections were carried out with either a Rigaku AFC6S diffractometer (for **1** and **8**) or an Enraf-Nonius CAD-4 automatic diffractometer (for **3**, **9** and **11**) using graphite-monochromatized Mo-Kα ($\lambda = 0.710\ 69$ Å) radiation. Intensity data were collected using the θ–2θ scan mode and corrected for absorption and decay. All data suffered different degrees of decay (see Table 2). Linear correction factors were applied in all cases. The structures were solved by SIR 92[21] (for **1** and **8**) or by MULTAN[22] (for **3**, **9** and **11**) and refined by full-matrix least squares on *F*. In the final cycles all non-hydrogen atoms were refined anisotropically and all hydrogen atoms were fixed at idealized positions. All calculations were carried out with a SGI R4000 computer using the TEXSAN program[23] (for **1** and **8**) or a microvax 3600 computer using the NRCVAX program[24] (for **3**, **9** and **11**). The hydrogen atoms of co-ordinated thf in complex **1** were not used due to the common disorder of this molecule. A summary of the data collection and structure solution is given in Table 2.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/376.

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