Asian Journal of Chemistry Vol. 5, No. 3 (1993), 563–567

Five Co-ordinated Organo Magnesium(II) Complexes of Triazene-1-Oxides†

RAMDHAR SHARMA*, A.K. THAKUR, S.N. CHAUDHARY‡ and S.B RAI**
Deptt. of Chemistry
R.D. & D.J. Post Graduate College,
Munger–811201, India.

Five co-ordinate complexes of organomagnesium(II) have been reported. Grignard reagents in (1 : 1) and (1 : 2) molar ratio interact with alcoholic solution of variedly substituted monobasic triazene-1-oxides to give complexes of the type $RMgT{\cdot}2H_2O$ and $RMgT_2$. The former complexes react with dipyridyl/o-phenanthroline to give complexes of the type RMgT·dipy/*o*-phen. The monodentate ligands such as pyridine, 2-picoline, 4-picoline, aniline and N-alkylaniline etc. on reaction with $RMgT{\cdot}2H_2O$ give complexes of the type RMgT·2L (L= monodentate ligands). In all the cases the co-ordination number of magnesium could be raised to a maximum of five. Failure to attain the usual six co-ordination for magnesium(II) appears to be due to the steric factors.

INTRODUCTION

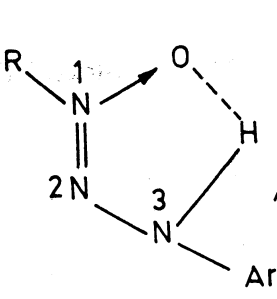
In continuation to our studies on the co-ordination compounds of magnesium(II)[1], we report the results of organomagnesium(II) complexes with variedly substituted monobasic bidentate/tridentate triazene-1-oxides TH(I), (II). The substituents of the triazene-1-oxides indicated by *o*-, *m*- and *p*- are counted from the N–C(Ar) bond. Dipyridyl, *o*-phenanthroline, 2-picoline, 4-picoline, aniline, N-alkylamine, THF, DMSO etc. have been used as secondary ligands. The co-ordination numbers of magnesium(II) are found to be six on the basis of n.m.r. studies with donors such as water, acetone and methanol[2]. The high charge : radius ratio of magnesium(II) also predicts a co-ordination number of six. Ligand ammonia has been found to give a five co-ordinate magnesium(II)[3]. Other five co-ordinate complexes of magnesium(II) reported[4] are $[Mg(OAsMe_3)_5](ClO_4)_2$ and approximately square pyramidal magnesium tetraphenylporphyrin hydrate.

EXPERIMENTAL

The Grignard reagent was obtained by following the published procedures[5]. Triazene-1-oxides were synthesised by the method of Elkins and Hunter[6], *i.e.*,

†Presented at 79th annual conference of Indian Science Congress Association at M.S. University, Baroda, India.

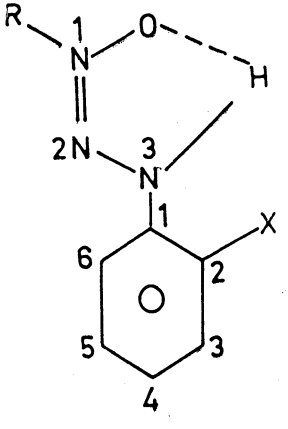
‡Department of Chemistry, J.R.S. College, Jamalpur (Munger), India.
**Department of Chemistry, Koshi College, Khagaria, India.



R=ALKYL,ARYL OR SUBSTITUTED ARYL.

Ar=ARYL OR SUBSTITUTED ARYL

I



= Ar

R = CH_3, C_2H_5, n-C_3H_7

X = F, Cl, Br I, OCH_3, OC_2H_5, SCH_3, $COOCH_3$, $COCH_3$

H

II

by coupling substituted hydroxyl amines with benzene diazonium chloride at 0–5°C using sodium acetate to control pH. The *ortho*-aryl substituted triazene-1-oxides were obtained by the method of Chakravorty[7]. While the Grignard reagent was used *in situ*, the crude products of triazene-1-oxides were crystallised from ethanol or aqueous-ethanol. The complexes were obtained by interacting Grignard reagent with triazene-1-oxides in 1 : 1 and 1 : 2 molar ratios. The product $RMgT{\cdot}2H_2O$ obtained by interacting RMgI and TH in 1 : 1 molar ratios gave the product $RMgT{\cdot}2H_2O$. This on interaction with dipy/*o*-phen gave the product RMgT·dipy/*o*-phen while the interaction with monodentate ligands (L) gave the product RMgT·2L. The products were recrystallised from acetone and stored in a vacuum desiccator. In contact with moisture the complexes lose their stability. The complexes are stable for over a fortnight. Complexes have no sharp melting points. They decompose at 210–220°C.

Magnesium was determined as pyrophosphate[8] after decomposing the complexes with 1 : 1 HCl. Nitrogen was estimated by the method of Dumas and conductivity measurements were made in nitro-methane using Philip's conductance bridge. The molecular complexities were determined in freezing benzene.

C and H determination and I.R. spectra in the range of 4000–200 cm^{-1} were recorded in CsI discs at RSIC, Madras.

RESULTS AND DISCUSSION

Organo-magnesium(II) chelates of monobasic bidentate/tridentate triazene-1-oxides obtained by interacting in 1 : 1 molar ratios were of the type $RMgT{\cdot}2H_2O$ while the products obtained by the interaction in the ratio 1 : 2 were of the type $RMgT_2$. The *ortho*-substituted tridentate triazene-1-oxides gave the derivative conforming to the formula $RMgT_2$, $RMgT{\cdot}2H_2O$ and $RMgT{\cdot}H_2O$ react with bidentate dipy/*o*-phen and monodentate ligands(L) to give complexes of the type $RMgT{\cdot}$dipy/*o*-phen, $RMgT{\cdot}2L$ and $RMgT{\cdot}L$ (Table 1). $RMgT_2$ did not interact with monodentate ligands. Conductivity measurements and molecular weight

TABLE 1
CHARACTERIZATION DATA OF ORGANOMAGNESIUM(II) CHELATES OF TRIAZENE-1-OXIDES (TH) AND DIPY/*o*-PHEN AND MONODENTATE LIGANDS (L)

Sl. No.	Complex	Substituents (TH)		% Mg	% N	% C	% H
		R	Ar				
1.	$RMgT{\cdot}2H_2O$	CH_3	C_6H_5	9.89 (10.04)	17.32 (17.57)	44.98 (45.19)	7.20 (7.11)
2.	$RMgT{\cdot}2H_2O$	C_6H_5	C_6H_5	7.86 (7.97)	13.87 (13.95)	55.60 (55.81)	6.12 (6.31)
3.	$RMgT_2$	CH_3	C_6H_5	6.86 (6.80)	23.80 (23.82)	54.42 (54.39)	5.75 (5.71)
4.	$RMgT_2$	C_6H_5	C_6H_5	5.41 (5.39)	18.91 (18.87)	64.82 (64.71)	6.10 (5.58)
5.	RMgT·dipy	CH_3	C_6H_5	6.65 (6.62)	19.36 (19.33)	63.12 (62.98)	5.30 (5.24)
6.	RMgT-*o*–phen	CH_3	C_6H_5	6.30 (6.26)	18.32 (18.27)	65.83 (65.79)	5.54 (5.48)
7.	RMgT·2py	CH_3	C_6H_5	6.70 (6.64)	19.42 (19.39)	63.22 (63.15)	5.60 (5.54)
8.	RMgT·2(2–pic)	CH_3	C_6H_5	6.22 (6.17)	18.07 (17.99)	58.88 (58.61)	7.13 (6.94)
9.	RMgT·2Anil	CH_3	C_6H_5	6.23 (6.17)	18.18 (17.99)	58.92 (58.61)	7.21 (6.94)
10.	RMgT·2(N-methylaniline)	CH_3	C_6H_5	5.81 (5.78)	16.91 (16.86)	66.63 (66.50)	7.02 (6.98)
11.	RMgT·2THF	CH_3	C_6H_5	6.96 (6.91)	12.22 (12.10)	45.10 (44.95)	8.42 (8.35)
12.	RMgT·2DMSO	CH_3	C_6H_5	6.72 (6.68)	11.73 (11.69)	36.82 (36.76)	7.12 (6.96)

Values in parentheses indicate calculated ones.
RMgX (R = C_2H_5, X = I).

determinations show that the chelalets are neutral and monomer. I.R. spectra indicate the bonding of O and N donor atoms of H_2O, dipy/o-phen and monodentate ligands to magnesium in RMgT·dipy/*o*-phen and RMgT·2L. The lowering of N→O stretch and disappearance of $\overset{3}{N}$–H indicate the bidentate behaviour of triazene-1-oxide. In all the complexes the coordination number of organo-magnesium(II) has been found to be invariably five.

Both in organic and inorganic synthesis Grignard reagents (RMgX) are the most widely used reagent. C_2H_5MgI has been used as the Grignard reagent in the present study. N,N,N',N'-tetra-methylenediamine (TMED) has been found to give stable tetrahedral adducts. The structural determination of Grignard reagent has shown that the crystals are made of RMgX·n (solvent). This indicates that any donor group having stronger donor property will replace the solvent molecules and occupy the co-ordination position in its place. Grignard reagents are found to give quite a good number of adducts with fascinating structures[9].

$RMgT·2H_2O$, $RMgT_2$, RMgT·dipy/*o*-phen, RMg.2L organo-magnesium(II), chelates formulated as above are supported by analytical data, monomer molecular weight and non-conductance values. Further support to the above formulations is lent through IR studies in the range 4000–200 cm^{-1} in CsI discs (Table 2). A

TABLE 2

IR BANDS (cm^{-1}) OF TH, $RMgT·2H_2O$, $RMgT_2$, RMg·2L

Sl. No.	Complex	Substituents (TH)		ν^{3}_{N-H}	$\nu^{1}_{N\rightarrow O}$	ν_{M-N}	ν_{M-O}
		R	Ar				
1.	TH	CH_3	C_6H_5	3200 s	1300 s	—	—
2.	TH	C_6H_5	C_6H_5	3190 s	1295 s	—	—
3.	$RMgT·2H_2O$	CH_3	C_6H_5	—	1245 s	435 w	470 w
4.	RMgT·dipy	CH_3	C_6H_5	—	1240 s	430 w	465 w
5.	RMgT·*o*-phen	CH_3	C_6H_5	—	1235 s	425 w	465 w
6.	RMgT·2py	CH_3	C_6H_5	—	1240 s	430 w	470 w
7.	RMgT·2(2-pic)	CH_3	C_6H_5	—	1235 s	430 w	465 w
8.	RMgT·2Anil	CH_3	C_6H_5	—	1240 s	435 w	470 w
9.	RMgT·2THF	CH_3	C_6H_5	—	1245 s	430 w	465 w
10.	RMgT·2DMSO	CH_3	C_6H_5	—	1235 s	435 w	470 w

s = Sharp, w = Weak.

broad band at 3200 cm^{-1} indicates the stretch of hydrogen-bonded H_2O molecule. $\overset{3}{N}$–H band at 3200 cm^{-1} of the free ligand disappears after co-ordination indicating N–M bond. $\overset{1}{N}$→O stretch at about 1300 cm^{-1} is considerably lowered to 1240 cm^{-1} due to $\overset{1}{N}$→O→M electron drainage[10,11]. Characteristic bonds of co-ordinated dipy/*o*-phen at 730 cm^{-1}, 1170 $cm^{-1}$and 1420 cm^{-1} also appear in

RMgT·dipy/*o*-phen[12,13]. The weak bonds at 420–470 cm^{-1} which were absent in the free ligands may be assigned to M–O and M–N bonds[14]. S–O stretch at 1070–1030 cm^{-1} is lowered to 1020–980 cm^{-1}. RMgT·$2H_2O$ and RMgT·2L have been assigned a *trans* diaquo and *trans* dimonodentate ligands. A *cis*-configuration should have led to the splitting of H_2O stretch[15]. Since magnesium(II) in RMgX and its derivatives has a spherically symmetrical cone (ionic radius 0.78 Å) of non-bonding electrons the arrangement of ligands with five donor points round the magnesium(II) will generate trigonal bi-pyramidal stereochemistry. The usual co-ordination of magnesium(II) complexes instead of six may be due to the steric factors[16].

REFERENCES

1. R. Sharma, A.K. Thakur and S.B. Rai, *Asian J. Chem.*, **3**, 171 (1991).
2. N.S. Poonia and A.V. Bajaj, *Chem. Rev.*, **79**, 389 (1979).
3. F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, John Wiley & Sons, NY, 155 (1988).
4. Y.S. Ng, G.A. Rodley and W.T. Robinson, *Inrog. Chem.*, **15**, 303 (1976).
5. Y-H. Lai, *Synthesis*, 585 (1981).
6. M. Elkins and Hunter, *J. Chem. Soc.*, 1346 (1938).
7. P.S. Zacharias and A. Chakravorty, *Inorg. Chem.*, **10**, 1961 (1971).
8. A.I. Vogel, A Text Book of Inorganic Qualitative Analysis, Longmans Green & Co., 478 (1964).
9. D. Fenton, Comprehensive Co-ordination Chem., Pergamon Press, Oxford, 3(23), 158.
10. R.L. Datta and R. Sharma, *J. Inorg. Nucl. Chem.*, **42**, 1204 (1980).
11. _____, *J. Sci. and Ind. Res*, **40**, 715 (1981).
12. R.L. Datta and S.P. Banerjee, *J. Indian Chem. Soc.*, **51**, 497 (1974).
13. R.L. Datta and A. Bhattacharya, *J. Inorg. Nucl. Chem.*, **42**, 1205 (1980).
14. R.N. Prasad, Mithilesh Zindal, Mumta Jain and Madhulika Sharma, *J. Indian Chem. Soc.*, **67**, 791 (1990).
15. R.W. Jones, (Jr.) and R.C. Fay, *Inorg. Chem.*, **12**, 2599 (1973).
16. C.F. Well, Metal Chelation, Clarendon Press, Oxford, p. 34 (1977).

(*Received*: 25 November 1991; *Accepted*: 10 October 1992) AJC–486