Pyrazolyl Derivatives of Aluminium and Gallium

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A series of volatile, tricyclic derivatives, $[N_2C_3H_3{\cdot}MR_2]_2$ (where M = Al or Ga; R = H, D, Me, Et, or Cl) has been synthesised by reacting pyrazole with the appropriate aluminium or gallium precursor. The resulting dimeric compounds have been characterised by elemental analyses, molecular weight determinations, and by ^1H n.m.r. and mass spectroscopic measurements. In all cases a boat conformation for the six-membered ring of four nitrogen and two metal atoms is consistent with the experimental results.

The reactions of Group III alkyls and hydrido-compounds with ligands containing active hydrogen are known to produce adducts which readily eliminate hydrogen or alkane to yield co-ordinatively unsaturated intermediates. In the majority of cases these intermediates oligomerise to produce co-ordinatively saturated cyclic derivatives.[1-3] The present paper extends our investigations in this area to include reactions of pyrazole with numerous Group III compounds thereby producing the tricyclic derivatives of general formula $N_2C_3H_3{\cdot}MR_2]_2$ (where M = Al or Ga; R = H, D, Me, Et, or Cl).

Considerable attention has been devoted to the analogous boron compounds,[4,5] $[N_2C_3H_3{\cdot}BR_2]_2$, and the whole area of boron–pyrazole chemistry has recently been reviewed.[5] However, scant attention has been paid to the chemistry of pyrazole derivatives of the heavier Group III elements.[5,6]

TABLE 1

Physical properties and analytical data for pyrazolyl derivatives of aluminium and gallium

						Analytical data (%) Found						Required					
Compound	M.p. (t/°C)	Precursor	Reaction conditions	*M* Found	Degree of association, *n*	M	R,H or D	Cl	C	H	N	M	R,H or D	Cl	C	H	N
$N_2C_3H_3{\cdot}GaH_2$	44—45	Me_3NGaH_3	r.t.	278	2·00	50·2	1·45					50·2	1·44				
$(3,5\text{-}Me_2)\text{-}N_2C_3H_3{\cdot}GaH_2$	154—155	Me_3NGaH_3	r.t.	338	2·03	41·8	1·20					41·3	1·20				
$N_2C_3H_3{\cdot}GaD_2$		Me_3NGaD_3	r.t.	284	2·02	49·0	2·80					49·5	2·84				
$N_2C_3H_3{\cdot}GaMe_2$	50—51	Me_3Ga	r.t.	340	2·04	42·8			35·9	5·50	16·8	41·8			36·0	5·40	16·8
$N_2C_3H_3{\cdot}GaEt_2$	Liquid	Et_3Ga	r.t.	382	1·96	35·0			42·7	7·00	14·0	35·8			43·2	6·68	14·4
$N_2C_3H_3{\cdot}AlMe_2$	83·5—84·5	Me_6Al_2	r.t.	252	2·03	21·0	23·5					21·8	24·2				
$N_2C_3H_3{\cdot}AlEt_2$	Liquid	Et_6Al_2	r.t.	302	1·99	17·7	38·0					17·8	38·1				
$N_2C_3H_3{\cdot}Al(Me)Cl$	155—153	$Al_2Me_4Cl_2$	Reflux	292	2·02	18·2	10·0	24·5				18·7	10·4	24·5			
$N_2C_3H_3{\cdot}Al(Et)Cl$	63—65	$Al_2Et_4Cl_2$	Reflux	311	1·97	16·9	18·3	22·2				17·0	18·3	22·4			

The present compounds were prepared by reacting benzene solutions of the appropriate aluminium or gallium compound with a stoicheiometric amount of pyrazole in the same solvent at room temperature.

$$e.g.\ 2Me_3NGaH_3 + 2N_2C_3H_4 \longrightarrow [N_2C_3H_3{\cdot}GaH_2]_2 + 2Me_3N + 2H_2$$

$$2Me_3Ga + 2N_2C_3H_4 \longrightarrow [N_2C_3H_3{\cdot}GaMe_2]_2 + 2CH_4$$

In the majority of cases hydrogen or alkane elimination occurred at room temperature but if the rate of the reaction was slow at this temperature the benzene solution was heated under reflux for a few hours to complete the reaction. The extent of the reaction was monitored by observing the gradual disappearance of the N–H stretching frequency in the i.r. spectrum of the reaction mixture, as time progressed. In all cases the product was sublimed *in vacuo* after removal of solvent (and trimethylamine when present). Experimental data are summarised in Table 1. The mild conditions required for the formation of these cyclic aluminium and gallium compounds, compared to those necessary to produce the *pyrazaboles*,[4] follows the pattern established from previous studies.[1,3,7,8]

The compounds listed in Table 1 range from mobile liquids through to fairly high melting solids, and with the exception of the two gallium dialkyl derivatives are all air and moisture sensitive materials. The dimethyl- and diethyl-gallium compounds are, however, quite stable in the open air and remain unchanged after prolonged exposure to the atmosphere. It is well known[1] that the first alkyl group of R_3Ga compounds and their derivatives is very air and moisture sensitive but that the subsequent alkyl groups are much less prone to attack. The present gallium metallocycles are no exception and their reluctance to undergo hydrolysis necessitated C, H, and N analyses for these two compounds rather than the usual active alkyl group analysis (see Table 1). Both the $[N_2C_3H_3{\cdot}GaH_2]_2$ and $[N_2C_3H_3{\cdot}GaMe_2]_2$ derivatives showed a strong tendency to supercool and could exist indefinitely as liquids at room temperature. Addition of a single crystal of the compound to a sample of the supercooled liquid caused instant transition to the solid phase. The 3,5-dimethylpyrazolyl gallium dihydride derivative showed vastly

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[1] G. E. Coates and K. Wade, 'Organometallic Compounds: Vol. 1, The Main Group Elements,' 3rd edn., Methuen, London, 1967, ch. 3.

[2] A. Storr, B. S. Thomas, and A. D. Penland, *J.C.S. Dalton*, 1972, 326.

[3] A. Storr and B. S. Thomas, *J. Chem. Soc.* (*A*), 1971, 3850.

[4] S. Trofimenko, *J. Amer. Chem. Soc.*, 1967, **89**, 3165.

[5] S. Trofimenko, *Chem. Rev.*, 1972, **72**, 497.

[6] A. D. Barnovskii, O. Yu. Okhlobystin, O. A. Osipov, K. M. Yunusov, Yu. V. Kolodyazhnyi, L. M. Golubinskaya, and V. I. Svergum, Abstracts of the Fifth International Conference on Organometallic Chemistry, Moscow, U.S.S.R., 1971, Vol. II, p. 376.

[7] A. Storr, *J. Chem. Soc.* (*A*), 1968, 2605.

[8] N. N. Greenwood, E. J. F. Ross, and A. Storr, *J. Chem. Soc.* (*A*), 1966, 708.

superior hydrolytic stability to the corresponding unsubstituted compound. Thus, acid hydrolysis at room temperature over a period of several days produced *ca.* 30% of the active hydrogen (Ga–H) required for this compound, whereas the unsubstituted derivative, [$N_2C_3H_3$·GaH_2]$_2$, yielded stoicheiometric equivalents of active hydrogen almost instantaneously on room temperature acid hydrolysis. Shielding of the Ga–H units by the methyl groups on the pyrazolyl moieties must be responsible for this difference in behaviour. The 3,5-dimethylpyrazolyl derivative was eventually analysed for active hydrogen by a high temperature acid hydrolysis in a closed break-seal bulb.

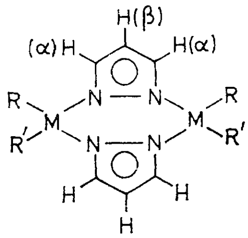
Mass Spectra.—The mass spectra of the two air stable dialkylgallium derivatives were recorded and in each case the data for the species in the gas phase confirmed the degree of association, *n*, obtained by cryoscopic measurements (Table 1). In both cases the parent ion was not observed and the strongest peaks in the spectra corresponded to loss of an alkyl group from the dimer ion. A similar absence of parent ions in the mass spectra of organo-aluminium compounds has been noted.[9,10]

The spectra of the two compounds showed that their fragmentation patterns, although very similar, displayed some noticeable differences. The spectrum of the diethyl compound showed that, in addition to stepwise loss of ethyl groups from the dimer ions, some fragmentation by loss of ethylene was also occurring. In this spectrum the ions produced by the stepwise loss of ethyl groups from the dimer units were the most abundant, [$Et_3Ga_2(N_2C_3H_3)_2^+$, rel. abund. 100; $Et_2Ga_2(N_2C_3H_3)_2^+$, 48; $EtGa_2(N_2C_3H_3)_2^+$, 28]. By comparison the spectrum of the dimethylgallium compound, [$N_2C_3H_3$·$GaMe_2$]$_2$, indicated that, after initial loss of one methyl group from the parent dimer to give the most abundant ion, $Me_3Ga_2(N_2C_3H_3)_2^+$, the next most favoured fragmentation path involved disintegration of the central six-membered ring with loss of a pyrazolyl moiety. The principal features of this latter mass spectrum, together with tentative assignments, are listed in Table 3. Fragments containing one gallium atom give rise to characteristic doublets with individual peaks at masses M and M + 2, the relative abundances of the peaks agreeing well with those predicted from the isotopic distribution of the metal atoms [^{69}Ga (60%); ^{71}Ga (40%)]. Species containing two gallium atoms give a series of three peaks at masses M, M + 2, and M + 4 with relative abundances again close to those anticipated from the isotopic distribution of the gallium atoms.

N.M.R. Spectra.—The ^{1}H n.m.r. spectra for the title compounds are summarised in Table 2. The pyrazolyl moieties exhibit a characteristic doublet : triplet pattern in all cases. The low field doublet (*J ca.* 2·2 Hz), of intensity 2, is assigned to the α-CH protons of the pyrazolyl group; the higher field triplet (*J ca.* 2·2 Hz), of intensity 1, to the β-CH groups. The signals due to the M–R groups occur at much higher field strengths, as indicated. The metal dialkyl derivatives give spectra suggesting magnetic equivalence of the M–R groups whereas the aluminium monoalkyl monochloro-derivatives give more complex patterns for the M–R groups suggesting more than one environment for the latter (see Table 2).

TABLE 2

^{1}H N.m.r. data for



compounds in [^{2}H$_6$]benzene solution

Compound			Pyrazolyl moiety		
M	R	R′	$\tau_{\alpha\text{-H}}$	$\tau_{\beta\text{-CH}}$	$\tau_{\text{M-R}}(\tau_{\text{M-R}'})$
Ga	H	H	2·69d	4·14t	
Ga	D	D	2·69d	4·14t	
Ga	Me	Me	2·61d	3·96t	9·97s
Ga	Et	Et	2·54d	3·87t	8·91t (β-CH_3), 9·37q (α-CH_2)
Al	Me	Me	2·54d	4·04t	10·34s
Al	Et	Et	2·46d	3·96t	8·93t (β-CH_3), 9·78q (α-CH_2)
Al	Me	Cl	2·51d 2·61d	4·24t	10·12s 10·26s
Al	Et	Cl	2·43d 2·53d	4·19m	8·92m (β-CH_3), 9·64m (α-CH_2)

TABLE 3

Mass spectrum of [$N_2C_3H_3$·$GaMe_2$]$_2$

m/e	Intensity	Assignment
321	40	
319	100	$Me_3Ga_2(N_2C_3H_3)_2^+$
317	59	
306	1·0	
304	2·3	$Me_2Ga_2(N_2C_3H_3)_2^+$
302	1·6	
291	2	
289	5	$MeGa_2(N_2C_3H_3)_2^+$
287	3	
254	17	
252	54	$Me_3Ga_2(N_2C_3H_3)^+$
250	40	
153	22	$MeGa(N_2C_3H_3)^+$
151	33	
138	4	$Ga(N_2C_3H_3)^+$
136	6	
101	20	Me_2Ga^+
99	30	
71	25	Ga^+
69	36	

The spectra listed in Table 2 are consistent with a tricyclic structure for the metallocycles, with a central six-membered ring of 4N and 2M atoms flanked by planar pyrazolyl rings to complete the molecular unit. Such an arrangement allows for delocalisation of 6π electrons in both pyrazolyl groups which gives an added stability to the tricyclic unit. Molecular models indicate that, rather than a planar array for the whole

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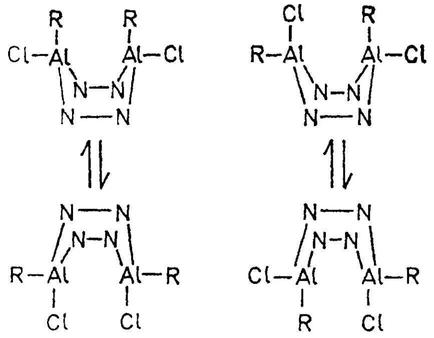
[9] B. D. Chambers, G. E. Coates, F. Glockling, and M. Weston, *J. Chem. Soc.* (*A*), 1969, 1712.

[10] Kathleen J. Alford, K. Gosling, and J. D. Smith, *J.C.S. Dalton*, 1972, 2203.

molecule, less strain exists about the M atoms if the central ring is in a boat conformation with the MR_2 moieties in bowspit positions. Such an arrangement has been confirmed recently for the solid $[N_2C_3H_3{\cdot}GaD_2]_2$ by *X*-ray crystallography techniques,[11] and for the remaining derivatives listed in Table 2 a similar boat conformation for the central ring, which rapidly inverts at room temperature in solution, would satisfactorily account for the observed ^1H n.m.r. spectra. Rapid inversion of the $M{-}(N{-}N)_2{-}M$ boat in solution is required to account for the spectra since a more static model would display signals corresponding to pseudo axial and pseudo equatorial groups on the M atoms. Thus, for example, the metal dimethyl derivatives show but one sharp singlet in the M–Me region of the spectrum which is not explicable on a 'static' boat conformation model. (Note: A planar tricyclic structure would give but one M–Me signal for these metal dimethyl compounds.) Low temperature ^1H n.m.r. measurements in carbon disulphide solvent to −100 °C on the $[N_2C_3H_3{\cdot}GaMe_2]_2$ compound gave no indication of resolving the unique singlet displayed at room temperature in the M–R region of the spectrum. Thus, even at this low temperature, inversion is sufficiently rapid to give apparent equivalence to the pseudo axial and pseudo equatorial methyl groups on the metal atoms.



(I) (II)

Possible conformers for $[N_2C_3H_3{\cdot}Al(R)Cl]_2$ dimers (C_3H_3 fragments of pyrazolyl rings omitted for clarity)

The two Al(R)Cl derivatives give ^1H n.m.r. spectra which suggest the existence of two isomers in solution. One isomer (I) has both R groups pseudo axial or pseudo equatorial (see Figure); the other isomer (II), has one R group pseudo axial and the other R group pseudo equatorial. The spectrum observed for the Al(Me)Cl compound, for example, is then explicable assuming a rapid inversion for both isomers in solution. The isomers would then each be expected to give a doublet for the α-CH groups of the pyrazolyl fragments and a singlet for the Al–Me groups. The observed spectrum (Table 2) of two doublets and two singlets in these particular regions of the spectrum is then accounted for. Some duplication of the β-CH triplet may also be anticipated but this was not resolved. The Al(Et)Cl derivative, likewise, displayed two well resolved doublets in the α-CH (pyrazolyl groups) region, but in this case the complexity of the Al–Et signals did not allow unequivocable assignment of different Al–Et groups. From the relative intensities of the two α-CH doublets in the spectra (roughly 2 : 1) it is evident that either isomer (I) or (II) must predominate in solution but at this stage it is not possible to predict which of the two isomers is favoured.

Solutions of both Al(R)Cl derivatives in carbon disulphide were cooled to slow down the rate of inversion of the $Al{-}({-}N{-}N{-})_2{-}Al$ ring in the hope that more complex ^1H n.m.r. spectra might be observed and thereby substantiate the boat conformation hypothesis. However, even at −90°, the pattern was unaltered, and again this suggests that a rapid inversion of the boat conformation must be taking place at these low temperatures.

The tricyclic structure proposed for these metallocycles, and established in the case of the $[N_2C_3H_3{\cdot}GaD_2]_2$ derivative, gives a canted arrangement to the pyrazolyl rings. (The angle between the planes through these rings in the $[N_2C_3H_3{\cdot}GaD_2]_2$ dimer is 127·4°.[11]) This configuration, together with the proposed availability of 6π electrons delocalised in each of the N_2C_3 rings, suggests the possibility of π-type interactions with suitable transition metal acceptor moieties, an area of investigation which is presently being explored.

EXPERIMENTAL

Materials were handled in a conventional high-vacuum line or in a glove box under an atmosphere of oxygen-free dry nitrogen. Benzene was dried by refluxing over molten potassium metal for several days, followed by distillation.

Starting Materials.—Pyrazole and 3,5-dimethylpyrazole were used as purchased (K and K Laboratories). Trimethylaluminium, triethylaluminium, dimethylaluminium chloride, and diethylaluminium chloride (Texas Alkyls) were vacuum distilled before use. Trimethylgallium,[12] triethylgallium,[13] trimethylamine–gallane [14] and -trideuteriogallane [14] were prepared as previously described.

Preparative Details.—The metallocycles synthesised in this work were all obtained by the same general procedure, which can be illustrated by the preparation of the gallane compound, $[N_2C_3H_3{\cdot}GaH_2]_2$.

Trimethylamine–gallane (1·0544 g, 8·00 mmol) was dissolved in benzene (50 ml) and the resultant solution was stirred whilst a benzene solution (50 ml) of pyrazole (0·5440 g, 8·00 mmol) was added dropwise at room temperature. A gas was vigorously evolved (presumed to be hydrogen) and after leaving the reaction mixture for about 1 h a sample was taken for a solution i.r. spectrum. The spectrum showed the total absence of any band in the N–H stretching vibration region and the reaction was deemed complete. After removal of solvent and trimethylamine from the product a white solid remained. This was

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[11] D. F. Rendle, A. Storr, and J. Trotter, *J.C.S. Chem. Comm.*, 1973, 189.

[12] A. Storr and B. S. Thomas, *Canad. J. Chem.*, 1970, **48**, 3667.

[13] A. W. Laubengayer and W. F. Gilliam, *J. Amer. Chem. Soc.*, 1941, **63**, 477.

[14] N. N. Greenwood, A. Storr, and M. G. H. Wallbridge, *Inorg. Chem.*, 1963, **2**, 1036.

vacuum sublimed and the sublimate analysed and subjected to physical measurements (Tables 1 and 2).

For the preparations of the metal alkyl derivatives the Group III precursor compounds, reacted with the pyrazole, are listed in Table 1. Also indicated in this Table is the reaction temperature.

Spectra.—^{1}H N.m.r. spectra were obtained on Varian HA 100 and T 60 instruments. The deuteriobenzene solutions were prepared in the glove box and the sample tubes sealed off to prevent oxidation and hydrolysis. All τ values are referred to benzene as τ (C_6H_6) = 2·84 p.p.m. [τ(Me_4Si) = 10·00 p.p.m.]. Low temperature ^{1}H n.m.r. spectra were recorded on carbon disulphide solutions prepared by vacuum transfer of purified solvent onto the metallocycle in the n.m.r. tube. The sample tube was again sealed off to avoid atmospheric interference. Mass spectra were recorded on a Varian MAT CH4 mass spectrometer at 70 eV with the inlet temperature at 60—80 °C. I.r. spectra were recorded on a Perkin-Elmer 457 spectrometer.

Molecular Weights.—Molecular weight determinations were conducted cryoscopically using benzene as solvent. The apparatus was designed to provide a nitrogen blanket over the solution to prevent atmospheric interference.[15]

Analysis.—The gallane and deuteriogallane samples were analysed for hydrolysable hydrogen (deuterium) as previously described for gallium hydride compounds.[14] The alkyl group content of the aluminium compounds was determined gas-volumetrically after hydrolysis with dilute acid. Chloride was determined by standard gravimetric procedures as silver chloride. In lieu of metal alkyl group analyses on the gallium alkyl derivatives, total C, H, and N analyses for these two compounds were obtained. Aluminium and gallium metals were determined gravimetrically as their 8-hydroxyquinolates.

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[15] A. Storr, Ph.D. Thesis, University of Newcastle upon Tyne, 1963.