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SYNTHESIS AND CHARACTERIZATION OF Me_3Ga AND Me_3In: ADDUCTS OF SECONDARY AMINES

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Abstract—The reactions of trimethylgallium and trimethylindium with a variety of secondary amines [$HNMe_2$, $HNEt_2$, $HNPr^n_2$, $HNPr^i_2$, $HNBu^n_2$, $HNBu^i_2$, $HNBu^s_2$, $HN(CH_2Ph)_2$, $HN(c\text{-}C_6H_{11})_2$, HNC_4H_8, HNC_5H_{10}, HNC_6H_{12} and $HN(CH_2CH_2)_2NMe$], produce a series of room-temperature stable liquid or solid adducts. These were characterized by ^1H and ^{13}C NMR, IR, mass spectrometry and elemental analysis. Spectroscopic comparisons are made between these and the corresponding trimethylaluminum derivatives. ^1H and ^{13}C NMR data for all three series of adducts indicate a correlation between the chemical shifts of the methyl groups on the metal and the relative steric requirements of the amines. The data show a general downfield movement of these chemical shifts with increasing steric bulk.

The chemical reactivity of organo-aluminium, -gallium and -indium compounds towards amines to form Lewis type adducts is well established.[1-6] Recently, there has been significant interest in this area of Group 13/15 chemistry, because these adducts may have potential applications in advanced materials synthesis and design.[7-9] Here, the use of primary or secondary amines is particularly advantageous, as the initially formed adducts can, upon heating, undergo elimination reactions to form condensed species.

Early work established the reactivity of $(Me_3Al)_2$,[10] Me_3Ga[11] and Me_3In[12] towards the simplest of secondary amines, Me_2NH, in the formation of datively bonded 1 : 1 adducts. Subsequently, the synthesis and characterization of several Me_3Al–secondary amine adducts has been reported.[13-16] However, only a few secondary amine adducts of Me_3Ga and Me_3In have been described in the literature. The chemical exchange properties of both $Me_3Ga \cdot HNMe_2$[17,18] and $Me_3In \cdot HNMe_2$[19] in solution have been examined using NMR. Stable adducts of Me_3Ga have been published for the secondary amines piperidine,[14] dicyclohexylamine,[20] 2,6-dimethylpiperidine[20] and thiomorpholine.[16] Similarly, adducts of Me_3In with dicyclohexylamine, 2-,6-dimethylpiperidine and 2,2,6,6-tetramethylpiperidine have been reported.[21] Additionally, the adducts $Me_3Ga \cdot HNEt_2$,[22] $Me_3Ga \cdot HNPr^i_2$[23] and $Me_3In \cdot HNPr^i_2$[24] have been briefly mentioned in the literature.

Recently, the synthesis and characterization of a series of 11 adducts, $Me_3Al \cdot HR$, formed between trimethylaluminum and the secondary amines, HR, where R = Me_2N, Et_2N, Pr^n_2N, Pr^i_2N, Bu^n_2N, Bu^i_2N, C_4H_8N, $C_5H_{10}N$, $C_6H_{12}N$, $MeN(CH_2CH_2)_2N$ and $(PhCH_2)_2N$, was reported by this laboratory.[13] This study provided IR, NMR and EI-MS data on a homologous series of 11 Al—N adducts. Herein, we report the synthesis and characterization of 13 $Me_3Ga \cdot HR$ and $Me_3In \cdot HR$

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adducts and two additional Me_3Al adducts with $HN(c\text{-}C_6H_{11})_2$ and $HNBu^s{}_2$. Spectroscopic comparisons are made between these compounds and the corresponding $Me_3Al\cdot HR$ species. The resulting data permit us to compare bonding and structural changes as a function of the group 13 element and the amine moiety in the three homologous adduct series.

EXPERIMENTAL

All manipulations of compounds were performed under dry nitrogen using standard Schlenk and vacuum-line techniques, in addition to a Vacuum Atmospheres model HE-43 Dri-lab equipped with a model HE-493 Dri-train. Trimethylgallium was received as a gift from Morton Advanced Materials and was distilled under vacuum prior to use. Its purity was checked using NMR. Trimethylindium was purchased from Morton Advanced Materials. All of the amines used in this study were purchased from Aldrich Chemicals, Inc., with the exception of $Bu^i{}_2NH$ (Fluka) and Me_2NH (Matheson Gas Products). Amines were dried and distilled over KOH prior to use, except Me_2NH, which was dried over Na. Benzene-d_6 and toluene-d_8 were purchased from Aldrich Chemicals, Inc. and stored over molecular sieves.

^1H and ^{13}C NMR data (see Tables 1, 2 and 3) for all the adducts were recorded at room temperature on a Nicolet 300 MHz multinuclear FT NMR or a Bruker ARX 300 FT NMR spectrometer. All spectra were obtained in 0.2 M C_6D_6 solutions and were referenced to the solvent. The spectral data for $(Me_3Al)_2$, Me_3Ga and Me_3In were obtained under the same conditions for comparative purposes: $(Me_3Al)_2$: $\delta_H = -0.36$, $\delta_c = -7.18$; Me_3Ga: $\delta_H = -0.15$; $\delta_c = 1.27$; Me_3In: $\delta_H = -0.24$, $\delta_c = -0.24$ ppm. The NMR spectra of the amines were obtained under similar conditions.

To remain consistent with the previously reported Me_3Al adduct data,[13] the following numbering system is used for the NMR data. Position 1 is assigned to the carbon bound to the nitrogen in the alkyl derivatives and to the nitrogen bound to the metal in the cyclic amine derivatives. For the $HNBu^s{}_2$ derivatives (**7**), positions 2 and 4 are assigned to the $CHCH_3$ and $CHCH_2CH_3$ methyl groups, respectively. Position 7 is assigned to the exocyclic carbon for derivatives **8** and **13**. Normal aromatic ring numbering is used.

Low-resolution EI-MS data were obtained on a HP5986A GC/MS spectrometer operated at 70 eV with a 2400 V electron multiplier. Vapour phase samples were introduced directly into the probe.

Satisfactory C, H and N elemental analyses were obtained for all new compounds and for those previously uncharacterized in the literature. These data, which were obtained from E+R Microanalytical Laboratory, Inc., Corona, New York, are included as supplemental material. Melting points for the solid compounds were determined in sealed capillaries using a Thomas Hoover melting point apparatus and were not corrected.

A Nicolet IR/42 FT spectrophotometer was used in obtaining IR spectral data for the newly reported adducts, as well as for those adducts whose spectra were not previously reported. Liquid products were recorded as neat samples, while solid products were recorded as Kel-F/Nujol mulls on KBr plates. The IR (cm^{-1}) and melting point data are as follows:

$Me_3Al\cdot HNBu^s{}_2$ (**7a**). IR: 3257(w), 2937(vs), 2935(vs), 2883(vs), 2361(w), 2340(w), 1461(s), 1388(s), 1325(w), 1312(w), 1269(w), 1187(s), 1137(m), 1058(m), 1011(m), 988(w), 966(w), 927(w), 875(w), 836(w), 804(w), 772(w), 698(vs), 639(m), 586(w), 527(m), 477(w), 410(w).

$Me_3Al\cdot HN(c\text{-}C_6H_{11})_2$ (**9a**). IR: 3217(m), 3018(w), 2930(s), 2855(s), 2664(w), 1222(w), 1183(m), 1126(w), 1070(w), 1055(w), 1033(m), 973(w), 934(w), 895(w), 848(w), 702(s), 633(m), 583(w), 528(m), 463(w), 415(w).

$Me_3Ga\cdot HNMe_2$ (**1b**); m.p. 33°C.[11] IR: 3292(br; w), 2978(s), 2945(vs), 2916(s), 2853(s), 2816(s), 1469(vs), 1410(sh; w), 1377(s), 1291(w), 1255(w), 1192(s), 1180(vs), 1125(m), 1111(s), 1058(w), 1024(s), 1004(vs), 981(m), 899(s), 728(s), 653(sh; w), 524(vs), 514(sh; m), 428(w).

$Me_3Ga\cdot HNEt_2$ (**2b**). IR: 3272(s), 2979(vs), 2943(vs), 2904(vs), 1469(s), 1457(s), 1386(s), 1190(vs), 1129(s), 1088(m), 1064(m), 1047(s), 989(vs), 844(m), 786(sh; m), 726(vs), 654(m), 543(vs), 512(s).

$Me_3Ga\cdot HNPr^n{}_2$ (**3b**). IR: 3274(s), 2969(br; vs), 2939(vs), 2879(vs), 1471(vs), 1460(sh; m), 1426(sh; m), 1385(m), 1343(w), 1311(w), 1264(w), 1247(w), 1190(vs), 1125(m), 1077(s), 1018(s), 947(s), 726(vs), 654(sh; m), 543(vs), 513(m).

$Me_3Ga\cdot HNPr^i{}_2$ (**4b**). IR: 3261(m), 2973(br; vs), 1468(sh; s), 1458(vs), 1428(m), 1389(vs), 1377(vs), 1354(sh; m), 1338(m), 1305(m), 1191(vs), 1159(sh; vs), 1147(vs), 1114(m), 1090(m), 1021(s), 975(s), 911(s), 727(vs), 659(s), 544(vs), 513(sh; s).

$Me_3Ga\cdot HNBu^n{}_2$ (**5b**). IR: 3274(m), 2962(vs), 2936(vs), 2876(vs), 1466(s), 1381(m), 1190(s), 1125(w), 1078(m), 1035(m), 932(w), 917(w), 890(w), 830(sh; w), 731(vs), 655(s), 543(vs), 513(sh; s).

$Me_3Ga\cdot HNBu^i{}_2$ (**6b**). IR: 3303(w), 2962(br; vs), 2875(vs), 1470(vs), 1420(s), 1395(s), 1372(s), 1190(vs), 1137(w), 1065(vs), 1036(s), 982(s), 968(sh; w), 929(s), 899(w), 808(w), 724(vs), 652(m), 544(vs), 513(sh; m).

Me$_3$Ga·HNBu$^s_2$ (**7b**). IR: 3265(w), 2968(vs), 2938(vs), 2880(s), 1496(s), 1420(s), 1351(w), 1328(w), 1266(s), 1171(m), 1142(m), 1045(m), 1013(m), 996(m), 929(w), 876(w), 836(w), 667(vs), 656(m), 513(s), 473(m), 409(w).

Me$_3$Ga·HN(CH$_2$Ph)$_2$ (**8b**); m.p. 62°C. IR: 3274(m), 3088(m), 3066(m), 3028(s), 2943(m), 1456(vs), 1377(s), 1366(sh; m), 1188(m), 1173(m), 1056(m), 1036(m), 1028(s), 987(m), 928(s), 728(s), 698(vs), 552(s), 538(s), 517(sh; m), 499(sh; m).

Me$_3$Ga·HN(c-C$_6$H$_{11}$)$_2$ (**9b**); m.p. 81–83°C (lit.[20] value 78–79°C). IR: 3242(m), 2936(s), 2857(s), 1215(w), 1191(vs), 1115(w), 1080(m), 1069(m), 1020(w), 977(w), 932(m), 895(w), 846(w), 725(vs), 668(s), 658(w), 620(w), 543(vs), 516(w), 461(w), 410(w).

Me$_3$Ga·HNC$_4$H$_8$ (**10b**); m.p. 47°C. IR: 3252(br; w), 2942(br; s), 1461(m), 1377(m), 1348(sh; w), 1307(w), 1190(s), 1055(m), 938(w), 905(m), 725(vs), 653(sh; w), 546(vs), 513(sh; w).

Me$_3$Ga·HNC$_5$H$_{10}$ (**11b**); m.p. 46–47°C (lit.[14] value 38°C). IR: 3247(m), 2945(br; vs), 2860(sh; s), 1455(vs), 1377(s), 1267(m), 1192(s), 1087(m), 1047(m), 1024(m), 986(s), 940(m), 871(s), 811(w), 721(vs), 654(sh; w), 546(vs), 514(w).

Me$_3$Ga·HNC$_6$H$_{12}$ (**12b**); m.p. 62–64°C. IR: 3272(m), 2931(br; vs), 1457(vs), 1377(s), 1308(w), 1289(w), 1191(s), 1174(sh; m), 1119(m), 1109(m), 1081(m), 1058(m), 1033(w), 995(m), 878(m), 820(m), 722(vs), 651(m), 546(vs), 512(sh; m).

Me$_3$Ga·HN(CH$_2$CH$_2$)$_2$NMe (**13b**); m.p. 81–82°C. IR: 3109(br; m), 2946(vs), 2809(vs), 2748(sh; m), 1455(vs), 1377(s), 1283(m), 1204(m), 1192(m), 1142(m), 1103(m), 1057(m), 1040(m), 908(m), 864(s), 721(vs), 544(vs), 514(sh; m).

Me$_3$In·HNMe$_2$ (**1c**); m.p. 13°C.[25] IR: 3297(s), 2995(s), 2956(vs), 2906(vs), 2842(s), 2811(w; sh), 1464(s), 1435(w), 1409(w), 1306(w), 1245(w), 1201(w), 1146(w), 1122(m), 1067(w), 1022(m), 967(m), 893(vs), 689(vs), 482(vs), 422(w).

Me$_3$In·HNEt$_2$ (**2c**). IR: 3273(m), 2976(vs), 2907(vs), 2842(s), 1478(m), 1457(s), 1392(s), 1362(w), 1172(m), 1148(s), 1108(m), 1092(m), 1066(m), 1047(m), 1027(w), 966(s), 909(w), 841(m), 814(m), 783(m), 689(vs), 481(vs), 434(m).

Me$_3$In·HNPr$^n_2$ (**3c**). IR: 3277(m), 2963(vs), 2906(s), 2878(s), 2842(m; sh), 1470(m), 1459(m), 1384(w), 1309(w), 1261(w), 1149(m), 1124(w), 1081(m), 1025(w), 1001(w), 935(w), 870(w), 849(w), 687(s), 482(vs).

Me$_3$In·HNPr$^i_2$ (**4c**). IR: 3261(w), 2972(vs), 2907(vs), 2842(s), 1476(m), 1430(w), 1389(s), 1376(s), 1347(m), 1307(w), 1145(s), 1090(m), 993(m), 964(s), 909(s), 838(w), 799(m), 772(w), 691(vs), 637(w), 479(vs).

Me$_3$In·HNBu$^n_2$ (**5c**). IR: 3277(w), 2959(vs), 2907(vs), 2874(s), 1465(m), 1380(m), 1343(w), 1312(w), 1149(m), 1083(m), 1016(w), 974(w), 912(m), 888(w), 830(w), 688(s), 481(vs), 430(w).

Me$_3$In·HNBu$^i_2$(**6c**). IR: 3307(s), 2958(vs), 2907(vs), 2873(vs), 1468(s), 1427(m), 1393(m), 1370(m), 1238(w), 1149(w), 1071(m), 1028(w), 976(m), 916(m), 895(m), 820(w), 803(w), 686(s), 481(s).

Me$_3$In·HNBu$^s_2$(**7c**). IR: 3266(w), 2968(vs), 2908(vs), 2879(s), 2361(w), 2340(w), 1462(s), 1385(s), 1264(w), 1148(m), 1036(w), 1012(w), 952(m), 877(m), 687(vs), 668(s), 479(vs).

Me$_3$In·HN(CH$_2$Ph)$_2$(**8c**); m.p. 47–48°C. IR: 3280(w), 3087(m), 3067(m), 3030(s), 2959(s), 2905(m), 2830(m), 1305(w), 1206(w), 1151(w), 1090(w), 1043(w), 1027(w), 978(w), 886(w), 868(w), 750(m), 699(s), 623(w), 486(s), 481(s), 417(w), 405(m).

Me$_3$In·HN(c-C$_6$H$_{11}$)$_2$(**9c**); m.p. 41–43°C (lit.[21] value 43–45°C). IR: 3249(w), 2934(s), 2857(s), 1301(w), 1264(w), 1208(w), 1152(m), 1091(m), 1073(m), 975(w), 932(m), 891(w), 841(w), 784(w), 688(s), 635(w), 483(s).

Me$_3$In·HNC$_4$H$_8$(**10c**); m.p. 33°C. IR: 3255(m), 2957(vs), 2905(vs), 2838(s), 2272(w), 1459(m), 1402(w), 1338(w), 1287(w), 1230(w), 1205(w), 1146(w), 1101(w), 1055(m), 923(m), 902(s), 691(vs), 483(vs).

Me$_3$In·HNC$_5$H$_{10}$(**11c**); m.p. 38–41°C. IR: 3254(w), 2945(s), 2908(m), 2853(m), 1265(w), 1190(w), 1150(w), 1088(w), 1047(m), 1020(m), 969(m; br), 939(m), 867(s), 845(w), 809(w), 686(s; br), 484(s).

Me$_3$In·HNC$_6$H$_{12}$(**12c**); m.p. 43–45°C. IR: 3277(w), 2948(s), 2858(m), 1310(w), 1290(w), 1198(w), 1124(w), 1079(w), 1046(w), 1033(w), 998(w), 965(w), 875(w), 835(w), 817(w), 686(m), 577(w), 484(s).

Me$_3$In·HN(CH$_2$CH$_2$)$_2$NMe (**13c**); m.p. 62–64°C. IR: 3114(m; br), 2950(s), 2907(s), 2860(m), 2807(s), 1525(w), 1485(w), 1452(m), 1284(w), 1195(w), 1141(w), 1107(w), 1035(w), 998(m), 966(w), 905(w), 864(w), 778(w), 678(m), 482(m), 427(w).

Synthesis of Me$_3$Al·HNBu$^s_2$(**7a**) *and* Me$_3$Al·HN(c-C$_6$H$_{11}$)$_2$ (**9a**)

To a hexane solution (5 cm^3) of (Me$_3$Al)$_2$ (2.00 g, 13.8 mmol) was slowly added a hexane solution (3 cm^3) containing an equal molar amount of the amine. Upon concentration by solvent removal, **9a** crystallized as a white solid (m.p. 110–112°C) and

7a was obtained as a clear colourless liquid. Essentially quantitative yields resulted.

General synthesis of $Me_3Ga\cdot$*secondary amine adducts*

In a typical synthesis, Me_3Ga (2.00 g, 17.4 mmol) was vacuum transferred on to the respective amine [$HNMe_2$, $HNEt_2$, $HNPr^n{}_2$, $HNPr^i{}_2$, $HNBu^n{}_2$, $HNBu^i{}_2$, $HNBu^s{}_2$, $HN(CH_2Ph)_2$, $HN(c\text{-}C_6H_{11})_2$, HNC_4H_8, HNC_5H_{10}, HNC_6H_{12} and $HN(CH_2CH_2)_2NMe$] (17.4 mmol), which was previously cooled to $-70°C$. The mixture was then slowly warmed to room temperature with reaction and adduct formation occurring at $-20°C$, which is the melting point of Me_3Ga. Liquid products were used without further purification. Solid products were vacuum sublimed (10^{-3} torr) at 30–50°C, with the exception of $Me_3Ga\cdot HNMe_2$, which was vacuum sublimed at room temperature using a cold finger cooled to $-20°C$. Yields for the solid products were in excess of 90% after sublimation.

General synthesis of $Me_3In\cdot$*secondary amine adducts*

In a typical synthesis, Me_3In (1.50 g, 9.38 mmol) was dissolved in pentane (5 cm^3). To this solution was added a pentane solution (3 cm^3) containing an equal molar amount of the amine. After mixing, the solution was filtered through a glass frit. The solution was then stirred and the pentane was removed under vacuum, leaving clear colourless liquids or white crystalline solids in nearly quantitative yields. The products were used without further purification.

RESULTS AND DISCUSSION

Reactions of Me_3M (M = Al, Ga, In) *with amines*

Me_3Al, Me_3Ga and Me_3In readily form adducts with the 13 secondary amines used in this study. All the adducts (**1**–**13**), which were isolated as discrete compounds, are listed in Table 1. Compounds **1c** and **2**–**7** exist as clear liquids, while the remaining compounds are sublimable white solids. The compounds are very air- and moisture-sensitive. Although compounds **1b**, **9b**, **11b**, **1c** and **9c** have been previously reported with ^1H NMR data, the ^1H NMR data were obtained under the solvent, concentration and temperature conditions used for all adducts in this study.

^1H *and* ^{13}C *NMR spectral data*

A comparison of the ^1H and ^{13}C NMR chemical shift data for the adducts, the parent amines and Me_3M, gives insight into the influence of steric interactions and the nature of the metal on the chemical shift values. In the case of the methyl groups on Al, Ga and In, the ^1H and ^{13}C chemical shift values (Table 1) are upfield from TMS for the adducts, with the exception of **7c** and **9c**, and are dependent upon the metal and the steric demands of the amine moiety. For the Ga and In adducts, the ^{13}C chemical

Table 1. Me_3M (M = Al, Ga, In) ^1H and ^{13}C NMR data for the group 13-amine adducts

		^1H (ppm)			^{13}C (ppm)		
Amine	Number	Al[a]	Ga	In	Al[a]	Ga	In
$HNMe_2$	**1**	−0.59	−0.29	−0.19	−9.69	−7.12	−8.78
$HNEt_2$	**2**	−0.49	−0.18	−0.11	−8.20	−5.22	−7.31
$HNPr^n{}_2$	**3**	−0.45	−0.15	−0.08	−8.27	−5.38	−7.28
$HNPr^i{}_2$	**4**	−0.36	−0.05	−0.01	−5.35	−2.01	−3.93
$HNBu^n{}_2$	**5**	−0.43	−0.14	−0.07	−8.21	−5.30	−7.21
$HNBu^i{}_2$	**6**	−0.42	−0.12	−0.06	−8.30	−5.38	−7.19
$HNBu^s{}_2$	**7**	−0.34[b]	−0.05	0.00	−5.68[b]	−2.32	−4.07
$HN(CH_2Ph)_2$	**8**	−0.38	−0.10	−0.11	−8.06	−5.10	−6.68
$HN(c\text{-}C_6H_{11})_2$	**9**	−0.31[b]	−0.01	0.04	−5.24[b]	−1.88	−3.64
HNC_4H_8	**10**	−0.52	−0.23	−0.13	−9.45	−6.78	−8.69
HNC_5H_{10}	**11**	−0.48	−0.19	−0.12	−9.37	−6.91	−8.63
HNC_6H_{12}	**12**	−0.46	−0.16	−0.09	−9.14	−6.47	−8.18
$HN(CH_2CH_2)_2NMe$	**13**	−0.48	−0.23	−0.13	−9.41	−6.85	−8.25

[a] Data obtained from reference 7 except where noted.
[b] This work.

shift values of these methyl groups shift upfield upon adduct formation. Figure 1 indicates a good correlation of methyl ^{13}C chemical shift data for the Ga and In adducts relative to those of the Al adducts. For any particular amine, the order of increasing downfield ^{13}C chemical shift value is Al < In < Ga. The order of magnitude of increasing downfield shift for a particular amine is approximately that observed for the parent Me_3Ga and Me_3In. No comparison can be made with trimethylaluminum, because it exists as a dimer in benzene solution. Although not shown, an analogous plot of the corresponding ^1H data indicates a similar trend, wherein the order of increasing downfield ^1H chemical shift is Al < Ga < In. This order, with the Me_3Al adduct chemical shifts being furthest downfield, has been observed for other Me_3M (M = Al, Ga, In) amine adducts.[26,27] The linearity of these plots suggests that stable adducts are formed in solution even with the more sterically demanding amines and that any contributions from dissociative exchange equilibria are the same regardless of the nature of the amine.

Figure 1 also suggests that, regardless of the nature of the metal, the methyl ^{13}C chemical shift values are shifted to lower field with the general increasing steric demands of the bound amine. For example, with $HNMe_2$ (**1**), the δ_c values are the farthest upfield, followed by the cyclic secondary amines (**10**–**13**), then the amines containing secondary carbons at the C(1) position (**2**, **3**, **5**, **6** and **8**), and finally those containing tertiary C(1) carbons (**4**, **7** and **9**). ^{13}C NMR chemical shifts are known to be very sensitive to steric effects.[13,28] The observed progressive downfield shift in chemical shift with increasing steric bulk on the ligand coordinated to a group 13 metal has been explained in terms of increasing *p* character of the M—C bond as the C—M—C bond angles decrease to accommodate larger ligands. Such trends have been observed for $Me_3Al \cdot PR_3$,[29] $[Me_2AlOR]_n$,[30] $[Me_2AlNR_2]_2$[13] and $[Bu^t_2GaOR]_2$[31] derivatives.

In an attempt to correlate the ^{13}C NMR chemical shift data with amine steric size, we have used amine cone angle (θ) data[32,33] for the free amine. Available cone angle data vs Me—M (M = Al, Ga, In) ^{13}C NMR chemical shift values, which are plotted in Fig. 2 for the three homologous adduct series, indicates a greater downfield ^{13}C chemical shift with increasing amine cone angle, with the Bu^i, Bu^s and CH_2Ph derivatives being exceptions. For the latter, the ^{13}C shift data appear to suggest that the effective cone angles in the amine moieties of **6**, **7** and **8** are much less (*ca* 125°, 134° and 127°, respectively) than the calculated values for the free amines (138°, 158° and 140°). Possibly, the cone angles of these amines, by analogy to phosphines that have large internal degrees of freedom, can decrease under steric strain.[29,34] Barron[29] obtained a similar result for $Me_3Al \cdot P(CH_2Ph)_3$, which he related to a possible reduction in the phosphine cone angle due to steric repulsion. Thus, from Fig. 2, we could infer that the greatest steric strain occurs in **4**, **7** and **9** with effective cone angles of *ca* 136° compared with the calculated values of 133°, 137° and 158°, respectively. This is followed by less steric strain in **2**, **3**, **6** and **8**, i.e. those with secondary carbons attached to nitrogen, and then **11** (cyclic amine) and **1**. A similar correlation of ^1H NMR chemical shift values with cone angle data occurs, although upfield

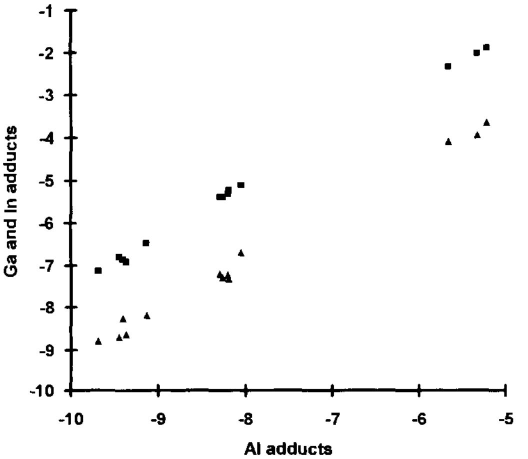

Fig. 1. M—Me ^{13}C NMR chemical shifts (ppm) for Me_3Al– vs. Me_3Ga– (■) and Me_3In– (▲) amine adducts. Compounds from left to right are in the following order of increasing chemical shifts: **1**, **10**, **13**, **11**, **12**, **6**, **3**, **5**, **2**, **8**, **7**, **4**, **9**.

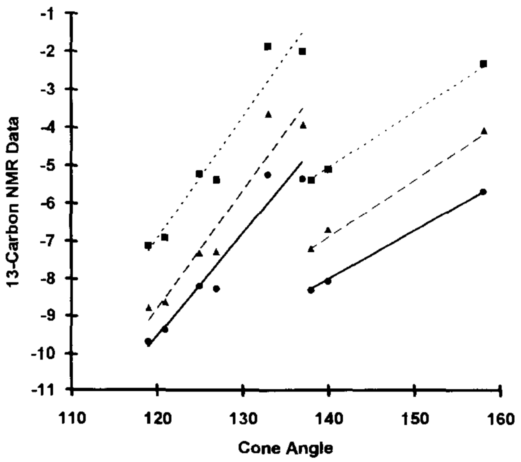

Fig. 2. M—Me ^{13}C NMR chemical shifts (ppm) for the Me_3Al– (●), Me_3Ga– (■) and Me_3In– (▲) amine adducts as a function of amine cone angle (θ). Compounds from left to right are in the following order of increasing cone angle: **1**, **11**, **2**, **3**, **9**, **4**, **6**, **8**, **7**.

shifts are observed with **4**, **6**, **7** and **8**, which have calculated cone angles > 132°. Barron[29] observed a similar trend with the phosphine adducts with the break occurring at phosphine cone angles > 150°. This upfield trend above a particular cone angle is explained by considering the shielding of the methyl groups on the metal by the most bulky ligand. Considering the expected shorter Al—N bond distance, the change toward upfield shifts should occur at a smaller cone angle in the amine adducts compared with the phosphine adducts.

The ^{1}H and ^{13}C NMR chemical shift data for all the adducted amine moieties are given in Tables 2 and 3, respectively. A comparison of the ^{13}C NMR chemical shift data for the parent amine and its Me$_3$M (M = Al, Ga, In) adduct gives information on steric interactions occurring in the adducts. Data in Table 4 indicate the differences that occur in ^{13}C chemical shifts at each carbon when the amine binds to the Me$_3$M group. In general, for each non-cyclic amine, the ordering of the magnitude of change is Al > Ga > In. The underscored entries in Table 4 denote the greatest upfield shifts in ^{13}C chemical shifts resulting from adduct formation. With **2**–**8**, these are found in the C(2) chemical shifts, which is indicative of a strong 1,3-diaxial interaction[13] between the Me$_3$M moiety upon binding to the nitrogen and the proton at C(2). Significant upfield shifts also are observed in the C(1) ^{13}C chemical shifts of the non-cyclic amines, except for the most sterically demanding cases (**4**, **7** and **9**). Here a notable downfield change in the ^{13}C chemical shift of C(1) results upon adduct formation. This would be consistent with the notion of significant conformational modifications, which give rise to effective amine cone angles that are much less than the calculated values for the unbound amine, occurring when the **4**, **7** and **9** amine moieties form adducts. Such changes in the cone angles should imply accompanying increases in the *p* character of the

Table 2. Amine ^{1}H NMR chemical shifts for Me$_3$Al, Me$_3$Ga and Me$_3$In adducts

Compound	N—H	H1	H2	H3	H4	H5	H6	H7
Me$_3$Al adducts								
7a	1.92	2.66	0.89	1.36	0.53			
9a	[a]	2.73	1.44	0.90	1.22	0.90	1.44	
Me$_3$Ga adducts								
1b	0.45	1.56						
2b	0.81	2.13	0.57					
3b	1.18	2.49	1.09	0.55				
4b	1.08	2.81	0.79	0.79				
5b	[a]	2.29	1.14	0.98	0.75			
6b	[a]	2.16	1.62	0.57	0.57			
7b	1.58	2.62	0.87	1.20	0.59			
8b	2.04		6.74	7.00	7.00	7.00	6.74	3.46
9b	1.45	2.61	1.58	1.05	1.20	1.05	1.58	
10b	1.23		2.15	0.98	0.98	2.15		
11b	[a]		2.25	0.79	0.95	0.79	2.25	
12b	1.08		2.37	1.01	1.01	1.01	1.01	2.37
13b	0.76		2.30	1.61		1.61	2.30	1.79
Me$_3$In adducts								
1c	0.20	1.58						
2c	0.55	2.08	0.62					
3c	0.87	2.15	1.15	0.60				
4c	[a]	2.63	0.77	0.77				
5c	0.90	2.22	1.16	1.00	0.76			
6c	1.45	2.12	1.65	0.58	0.58			
7c	[a]	2.48	0.83	1.18	0.59			
8c	1.81		7.00	7.00	6.78	7.00	7.00	3.37
9c	1.41	2.46	1.54	0.98	1.08	0.98	1.54	
10c	0.87		2.25	1.07	1.07	2.25		
11c	0.60		2.21	0.82	0.98	0.82	2.21	
12c	0.80		2.33	1.02	1.02	1.02	1.02	2.33
13c	0.63		2.33	1.62		1.62	2.33	1.82

[a] N—H peak not observed.

Table 3. Amine ^{13}C NMR chemical shifts for Me_3Al, Me_3Ga and Me_3In adducts

Compound	C1	C2	C3	C4	C5	C6	C7
Me_3Al adducts							
7a	53.14	18.58	28.57	10.93			
9a	56.01	32.56	25.50	25.87	25.50	32.56	
Me_3Ga adducts							
1b	37.11						
2b	41.51	12.42					
3b	50.06	20.94	11.26				
4b	46.89	21.91	21.91				
5b	48.12	29.91	20.37	13.85			
6b	57.48	25.86	20.02	20.02			
7b	53.05	19.04	28.89	10.95			
8b	136.70	129.14	128.77	128.30	128.77	129.14	51.82
9b	55.13	33.04	25.67	25.81	25.67	34.04	
10b		46.72	24.81	24.81	46.72		
11b		45.80	25.97	23.35	25.97	45.80	
12b		47.61	29.13	26.52	26.52	29.13	47.61
13b		43.86	54.33		54.33	43.86	45.09
Me_3In adducts							
1c	37.78						
2c	42.59	13.10					
3c	51.00	21.69	11.37				
4c	46.64	22.15	22.15				
5c	48.95	30.40	20.40	13.87			
6c	57.48	26.09	19.96	19.96			
7c	52.80	19.17	28.68	10.53			
8c	136.80	129.15	128.86	128.10	128.86	129.15	51.75
9c	54.70	32.74	25.48	25.77	25.48	32.74	
10c	47.16	25.04	25.04	47.16			
11c	46.54	26.25	23.68	26.25	46.54		
12c	48.26	29.57	26.61	26.61	29.57	48.26	
13c	45.23	55.06		55.06	45.23	46.14	

N—C bond as the C—N—C bond angles decrease. Figure 3 depicts the relationship between the ^{13}C NMR shifts (δ_c) of the carbon adjacent to the adducted nitrogen for the adducts with respect to the δ_c values for that carbon on the unbound amines. A dashed line (slope = 1, corresponding to data for the free amine) is included to assist the reader in noting the direction of the shifts occurring upon adduct formation. The linearity of the plot for all the adducts, except **4**, **7** and **9**, suggests that the nature of the adducts is consistent within each metal series.

In an attempt to determine if exchange was occurring with **4**, **7** and **9** or was significantly contributing to the observed chemical shifts of the adducts, variable-temperature (-80°C to room temperature) ^1H and ^{13}C NMR data were collected for compounds **1b** and **4b**. The $HNMe_2$ derivative (**1b**) was chosen to act as a control, based on the assumption that **1b** was not in equilibrium due to its small steric size and that dissociative exchange equilibrium was not previously observed for $Me_3Ga \cdot NMe_3$.[11] The chemical shifts measured in the variable-temperature study varied by <0.5 ppm over the temperature range. This result suggests that simple temperature dependence of the chemical shifts, not exchange equilibria, exists for **1b** and **4b** from $-80°$ to room temperature. This is consistent with the NMR data as discussed above.

IR data

Although direct comparisons of IR data for the homologous adduct series are limited by the difficulties in making specific peak assignments, a correlation of the distinctive N—H stretching vibration can be made. The observed N—H frequencies for the Al, Ga and In adducts are 30–180 cm^{-1} less than those for the free amines. Unfortunately, such comparisons are somewhat complicated by hydrogen bonding contributions occurring in the free amines. On the other hand, the

Table 4. Differences in ^{13}C NMR chemical shifts: δ(Me$_3$M·amine) − δ(free amine)

Compound	C1	C2	C3	C4	C5	C6	C7
Me$_3$Al adducts							
1a	−2.37						
2a	−3.19	−3.47					
3a	−2.64	−3.03	−0.95				
4a	1.69	−2.21	−2.21				
5a	−2.54	−3.44	−0.68	−0.62			
6a	−1.48	−3.22	−1.01	−1.01			
7a	1.88	−2.26	−2.00	0.52			
8a	−5.71	0.79	0.55	1.30	0.55	0.79	−1.81
9a	2.90	−2.28	0.01	−0.87	0.01	−2.28	
10a		−0.97	−1.13	−1.13	−0.97		
11a		−2.43	−2.10	−2.60	−2.10	−2.43	
12a		−2.69	−3.31	−1.02	−1.02	−3.31	−2.69
13a		−2.06	−2.63		−2.63	−2.06	−1.05
Me$_3$Ga adducts							
1b	−1.91						
2b	−2.80	−3.29					
3b	−2.19	−2.90	−0.82				
4b	1.61	−1.79	−1.79				
5b	−2.03	−3.06	−0.51	−0.46			
6b	−1.14	−3.13	−0.87	−0.87			
7b	1.79	−1.80	−1.68	0.54			
8b	−4.46	0.63	0.42	1.30	0.42	0.63	−1.59
9b	2.02	−1.80	0.18	−0.93	0.18	−1.80	
10b		−0.65	−1.02	−1.02	−0.65		
11b		−1.97	−1.57	−2.31	−1.57	−1.97	
12b		−2.00	−2.71	−0.85	−0.85	−2.71	−2.00
13b		−2.65	−2.53		−2.53	−2.65	−1.86
Me$_3$In adducts							
1c	−1.24						
2c	−1.72	−2.61					
3c	−1.25	−2.15	−0.71				
4c	1.36	−1.55	−1.55				
5c	−1.20	−2.57	−0.48	−0.44			
6c	−1.14	−2.90	−0.93	−0.93			
7c	1.54	−1.67	−1.89	0.12			
8c	−4.36	0.64	0.51	1.10	0.51	0.64	−1.66
9c	1.59	−2.10	−0.01	−0.97	−0.01	−2.10	
10c		−0.21	−0.79	−0.79	−0.21		
11c		−1.23	−1.29	−1.98	−1.29	−1.23	
12c		−1.36	−2.27	−0.76	−0.76	−2.27	−1.36
13c		−1.28	−1.80		−1.80	−1.28	−0.81

N—H stretching frequencies for the Me$_3$Al adducts can be compared with those for the corresponding Me$_3$Ga and Me$_3$In adducts. Plots of the N—H stretching frequencies for the Me$_3$Al adducts vs. those for the Me$_3$Ga and Me$_3$In adducts are linear in each case [Me$_3$Ga, ($R = 0.987$); Me$_3$In, ($R = 0.984$)].

The N—H stretches for the trimethylgallium adducts are shifted approximately 24 cm^{-1} and the trimethylindium adducts about 27 cm^{-1} towards higher frequencies compared with the Me$_3$Al adducts. For Me$_3$Ga·NH$_3$,[35] the N—H stretching frequency is 3277 cm^{-1} compared with 3254 cm^{-1} for Me$_3$Al·NH$_3$.[36] These trends suggest a direct influence of the group 13 metal on the N—H stretching frequency.[14]

MS data

The mass spectra for the trimethylaluminum adducts consistently displayed high intensity peaks

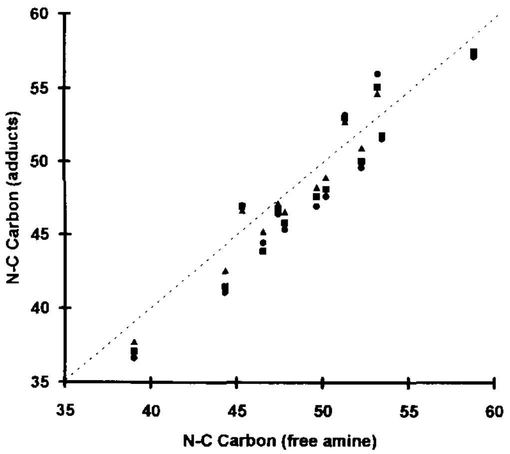

Fig. 3. N—C ^{13}C NMR chemical shifts (ppm) for the free amines vs. the Me_3Al– (●), Me_3Ga– (■) and Me_3In– (▲) amine adducts. Compounds from left to right are in the following order of increasing chemical shift of the carbon adjacent to the nitrogen for the free amines: **1**, **2**, **4**, **13**, **10**, **11**, **12**, **5**, **7**, **3**, **9**, **8**, **6**. The dashed line is for comparative purposes only (see text).

for $[M-15]^+$, due to loss of a methyl group from the adduct.[13] Molecular ion peaks were also observed for **2a** and **4a**. In contrast, very low intensity $[M]^+$ and $[M-15]^+$ peaks were observed for only a few of the Me_3Ga and Me_3In adducts. Instead, the most intense peaks were those associated with fragmentation of Me_3Ga, Me_3In and the amines. For example, the base peaks usually consisted of $[Me_2Ga]^+$ and $[Me_2In]^+$, which are the primary fragments observed for free trimethylgallium or trimethylindium.[37] This is consistent with the reported mass spectral data for other Me_3Ga[20] and Me_3In[21,38] amine adducts. These results suggest that, in the vapour phase, the Ga and In adducts either readily dissociate or that most of the metal–nitrogen bonds are easily broken upon electron impact. This is consistent with the known relative Lewis acidities of Me_3Al, Me_3Ga and Me_3In towards group 15 and 16 Lewis bases[39] and with the reported stabilities of $Me_3M \cdot NMe_3$ (M = Al, Ga, In) as reflected in their heats of adduct formation. Gas phase studies of $Me_3Ga \cdot NMe_3$[39] and $Me_3In \cdot NMe_3$[12,39] give ΔH values of -88 and -83.3 kJ mol^{-1}, respectively. Although $Me_3Al \cdot NMe_3$[15] is too stable to provide comparative data in the gas phase, solution studies give a ΔH value of -125 kJ mol^{-1}.

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