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Functional Group Reductions with Lewis Base Adducts of Gallane

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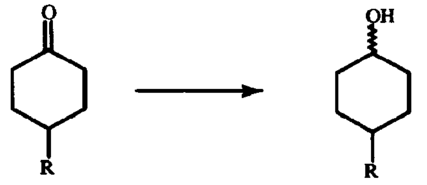
Abstract: Tertiary amine and tertiary phosphine adducts of gallane, L·GaH_3 (L = Me_3N, quinuclidine, $(C_6H_{11})_3P$), reduce a variety of unsaturated functional groups with a selectivity different to that observed for similar alane adducts.

A large number of structurally diverse boro-hydride and alumino- hydride reagents, including Lewis base adducts[1], have been examined for chemo- and stereo-selectivity in the hydrometallation of unsaturated functional groups. By comparison, the corresponding reactions of gallium hydrides have received very little attention. The unique structural and electronic properties of Lewis base adducts of gallane[2] coupled with preliminary findings of unusual reactivity[3] suggest that such compounds may exhibit selectivity different to that of existing reagents. In this report we compare the chemo-, regio- and diastereoselectivity of reduction with Lewis base adducts of gallane and some corresponding adducts of alane. In general, differences in chemistry relate to a tendency for aluminium (but not gallium) to form hypervalent structures, the frailty of Ga - H bonds relative to Al - H bonds, and the polarizing influence /back bonding participation of the d^{10} core for gallium[2].

The Lewis base adducts L·MH_3 (**1**, M = Al; **2** M = Ga; **3**, M = B; **a**, L = Me_3N; **b**, quinuclidine; **c**, $(C_6H_{11})_3P$) can be conveniently prepared either by salt elimination or ligand displacement[4]. Various reductions were performed with equimolar proportions of substrate and metal hydride in anhydrous toluene at room temperature (*ca* 16 hours, inert atmosphere) and then quenched with dilute acid. Product ratios were determined by ^1H NMR and / or GC analysis. The substrates studied are those commonly used to evaluate the chemical properties of reducing agents[1].

Reduction of 4-t-butylcyclohexanone with equimolar proportions of quinuclidinealane (**1b**), quinuclidinegallane (**2b**) or tricyclohexylphosphinegallane (**2c**) (Scheme 1) was quantitative and resulted in a predominance of the *trans* alcohol in each case.



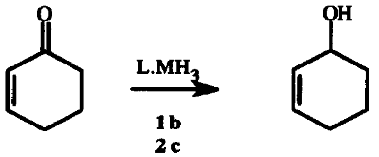
R	L.MH3	% trans	% cis
t-Bu	**1b**	83	17
t-Bu	**2b**	87	13
t-Bu	**2c**	85	15
COOEt	**2b**	70	30

Scheme 1

The diastereoselectivity observed is similar to that of many other alumino- and borohydride reagents[1] and is consistent with the Cieplak model involving stabilisation of the transition state by antiperiplanar allylic bonds[5]. Decreasing the amount of the quinuclidine metal hydrides **1b** or **2b** to 0.33 molar equivalents had little effect on the diasteroselectivity although reduction with the latter proceeded only to 72% completion which is consistent with two reactive hydrogens under these conditions. Changing the gallane ligand from quinuclidine to tricylohexylphosphine also had a negligible effect on the diastereoselectivity of reduction.

No ester reduction was observed in the reaction of ethyl 4-oxocyclohexanecarboxylate (Scheme 1, R = COOEt) with quinuclidinegallane (**2b**) or on reaction of ethyl benzoate with trimethylaminegallane (**2a**). By comparison, trimethylaminealane (**1a**) reduced ethyl benzoate to benzyl alcohol in 80% yield under these conditions.

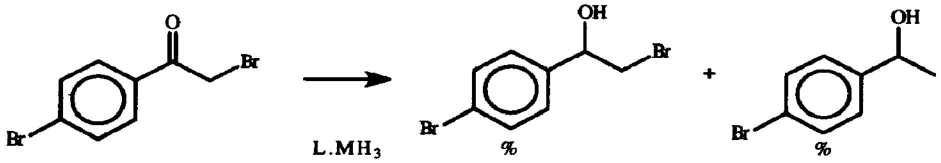
Both alane **1b** and gallane **2c** reduced 2-cyclohexenone to the allylic alohol quantitatively (Scheme 2).



Scheme 2

The absence of any observable conjugate addition indicates that both reagents are relatively "hard" reducing agents on the HSAB scale[6].

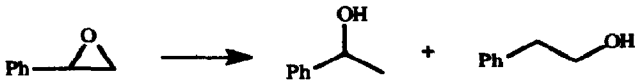
Trimethylaminegallane (**2a**) reduced 4-bromophenacyl bromide without significant debromination. The corresponding borane **3a** was unreactive under these conditions and alane **1b** reduced the carbonyl group predominantly with concomitant cleavage of the adjacent carbon - bromine bond (Scheme 3).



$L.MH_3$	%	%
1b	7	93
2a	94	6
3a	--	--

Scheme 3

These results are consistent with the increased electronegativity of gallium (and the associated decreased reactivity of the less polar M - H bond) relative to aluminium[2]. This difference was also reflected in the regiochemistry of styrene oxide reduction (Scheme 4).



L.MH3	%	%
1b	63	37
2c	>99	<1 (47% conversion)

Scheme 4

The significant proportion of 2-phenylethanol produced in the reaction of alane **1b** suggests oxygen - aluminium coordination as the primary process with positive charge development at the benzylic carbon prior to hydride transfer[7]. A very similar product distribution has recently been reported for the corresponding reaction of $Et_3N{\cdot}AlH_3$[8]. By comparison, reduction with gallane **2c** resulted in exclusive formation of the secondary alcohol (albeit in only 47% conversion under these conditions). Reduction of this substrate with $LiAlH_4$ yields the secondary alcohol predominantly[7] whereas the opposite regiochemistry is observed with more electropositive reagents such as $LiAlH_4$ / $AlCl_3$[7] and BH_3 / BF_3[9] which is consistent with our findings.

This preliminary investigation indicates that Lewis base adducts of gallane reduce a variety of functional groups and with a selectivity different to that of Lewis base adducts of alane. Overall, they appear to be less reactive, "softer" reducing agents than the corresponding class of alanes, as expected from electronegativity and bonding considerations[2]. While the selectivity observed with each of the above substrates could be achieved or exceeded with other boro-hydride and alumino- hydride reagents, we are unaware of any other reagent with the same overall reduction characteristics. Lewis base adducts of gallane should, therefore, be considered candidates for further study in the quest for new, selective reducing agents.

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