Reactions of Organohalogenometalates

The triorganometallanes R_3M of group 13 metals are distinct lewis acids. The electrophilic reactivity is decreased by using coordinating donor solvents, an intrinsic problem, which limited the chemistry of this field for some time. However, the effect can be used. Binuclear alkylaluminum alcoholates show very high reaction rates in the nucleophilic addition to carbonyl compounds. The carbonyl function is activated in the known manner and the organic ligand is transferred in a 1,2 fashion [1].
Aluminumorganyls are especially known for carbaluminination and hydroalumination, which are regioselective using alkynes and additionly stereoselective using alkenes by severe cis-addition [2]. Related to this is the formation of aluminumketimids from nitril adducts of the triorganoalanes [3]:

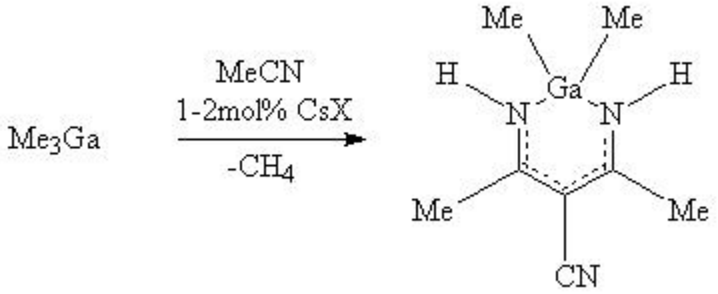
$$2\,[R_3M(NCR')] \;\circledR\; [R_2MNC(R')R]_2$$

The reaction works at 80°C for primary and secondary nitrils. The lewis acidic character is also shown in the ligand distribution reaction of metallanes and group 13 halides [4]:

$$2\,R_3M + MX_3 \;\circledR\; 2\,R_2MX \quad \text{or} \quad R_3M + 2\,MX_3 \;\circledR\; 2\,RMX_2$$

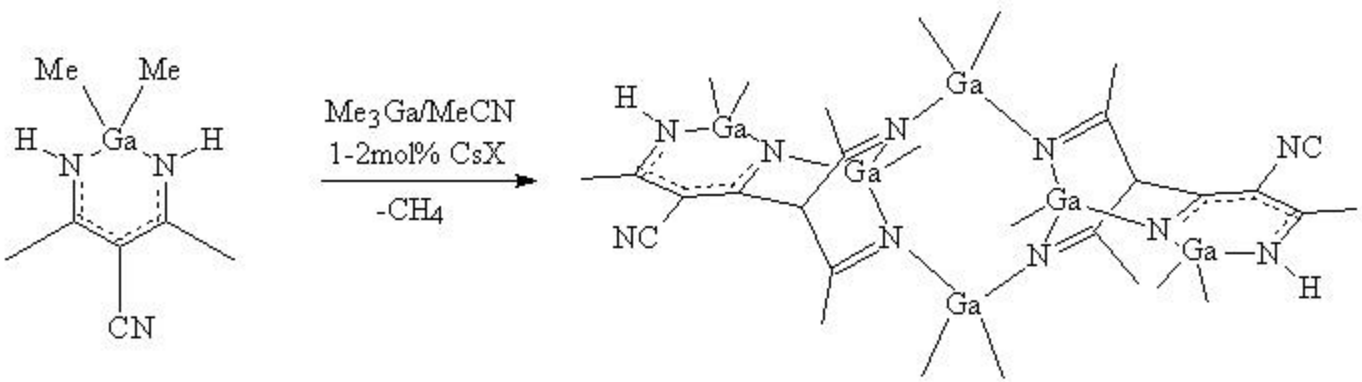
These reactions suggest the character of a species $X_2M\text{-}X\text{-}MR_3$, which transfers a ligand X^- or R^-.
In contrast to the metallanes the organohalogenometalates exhibit a significant basic character. In a synergetic effect both the acidic property of a metallane and the basic property of a metalate can be used for condensation reactions of nitrils [5]. Trimethylgallium does not react with acetonitril at room temperature or even at 90°C. Adding 1-2 mol% of a cesium halide CsX (X = F, Cl, Br) to mixtures of $Me_3Ga/MeCN$ the solutions become

yellow and after some time dark brown. Within 48 h at 65°C compound **1** is formed in a 62% yield:

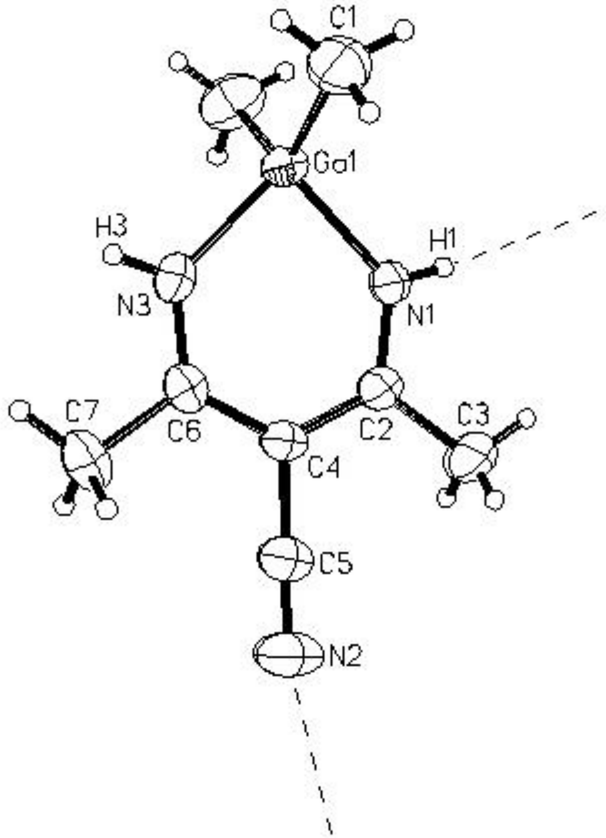


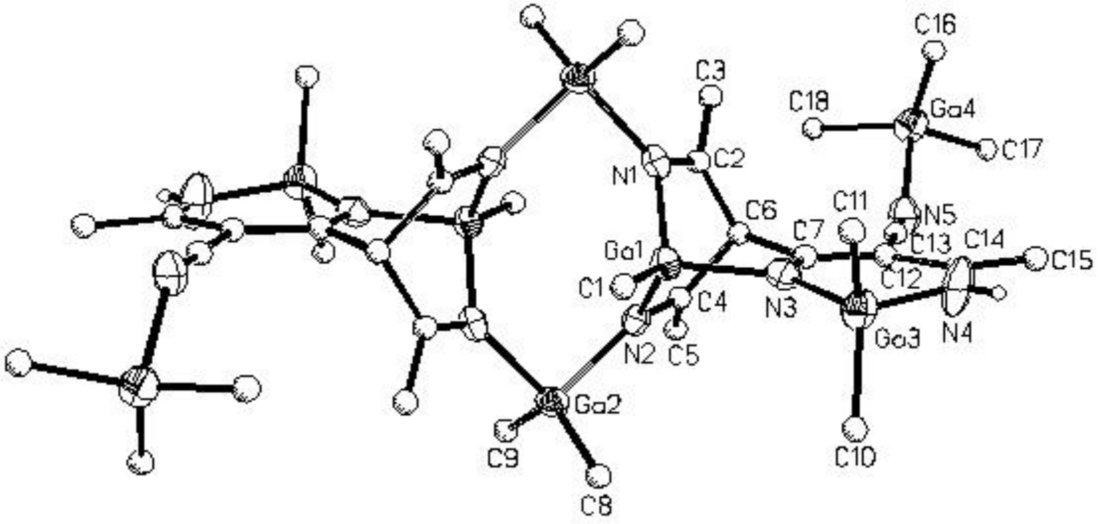
1

Changing the reaction patterns time and temperature compound **2** can be synthesized. The sixnuclear complex possibly marks the way to a insoluable polymer which is the result of reaction times higher than 90 h under reflux conditions.



2


C1
Ga1
H3
H1
N3
N1
C7
C6
C2
C3
C4
C5
N2



Structures of the compounds **1** and **2***2GaMe$_3$

Literature:

1: T. Ooi, M. Takahashi, K. Maruoka, *Angew. Chem.* **1998**, *110*, 875.
2: J. J. Eisch, C. K. Hordis, *J. Am. Chem. Soc.* **1971**, *93*, 2974. J. J. Eisch, C. K. Hordis, *J. Am. Chem. Soc.* **1971**, *93*, 4496.
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4: J. J. Eisch, *J. Am. Chem. Soc.* **1962**, *84*, 3830.
5: M. R. Kopp, T. Kräuter, A. Dashti-Mommertz, B. Neumüller, *Organometallics* **1998**, *19*, 4226.