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CHEMISTRY OF
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Comment

Comment on "Methylmagnesium Alkoxide Clusters with Mg_4O_4 Cubane- and Mg_7O_8 Biscubane-Like Cores: Organometallic Precursors for Low-Temperature Formation of MgO Nanoparticles with Variable Surface Defects"

The paper on methylmagnesium alkoxides by Heitz et al.[1] is very interesting and involves some very difficult work. Contrary to the statements by Heitz et al.,[1] Ashby et al.[2] did not propose the heptameric $(RMgOR')_7$ cluster for methylmagnesium *n*-propoxide in benzene. That cluster was proposed by Hitchcock et al.,[3] and we actually took issue with their proposed structure. We[2] reported that the NMR spectrum was consistent with a single methyl environment (i.e., "sharp singlet at room temperature, and no other additional signals were observed at temperatures as low as -70 °C"). We then noted that "... the *n*-propoxy methyl group is more complex [in benzene] than observed in other solvents [ethers] ... [using a 60 MHz instrument]". Indeed, we went on to recommend X-ray crystallography to resolve the issues. The biscubane structure found by Heitz et al.[1] has one methyl site (all six methyl positions are equivalent) and two different *n*-propyl sites (six around hexa-coordinate Mg^{2+} and two bridging between three methyl-Mg units), which they were able to resolve using 200 and 400 MHz instruments. Thus, our[2] NMR suggests that we were working with the same biscubane reported by Heitz et al.,[1] and we find no support for a stable cluster heptamer structure as proposed by Hitchcock et al.[3]

It is noted that Heitz et al.[1] prepared their products (cubane and biscubane) by refluxing the initial product of dimethylmagnesium and the alcohol (1:1 mole ratio) in toluene (bp 111 °C) for 48 h. It is obvious that the biscubane structure $(R_6Mg_7OR'_8)$ has an excess of OR′ and deficiency of R relative to the cubane $(R_4Mg_4OR'_4)$. Thus, some sort of disproportionation or decomposition must occur in these reaction mixtures. As we reported,[2,4] the cubane $\mathrm{MeMgO}^{t}\mathrm{Bu}$ sublimes at 140 °C in vacuo without decomposition; $\mathrm{MeMgO}^{n}\mathrm{Pr}$ did not sublime when heated to 120−130 °C in vacuo but turned pale yellow and underwent a drastic change in its IR spectrum (Figure 1); and $\mathrm{MeMgO}^{iso}\mathrm{Pr}$ partially sublimes and partially decomposes at 100 to 105 °C in vacuo (Figure 2). The decomposition product is apparently MgO. Since we[2,4] observed solid $\mathrm{MeMgO}^{iso}\mathrm{Pr}$ to decompose at 105 °C, it is not surprising that their[1] yield of $\mathrm{MeMgO}^{iso}\mathrm{Pr}$ cubane was only 42% after refluxing in toluene (b.p., 111 °C), but the yields of the biscubanes were higher (e.g., 74−96%). I discussed the dynamics of cubane formation at some length in my 1974 thesis,[2,4] but work is needed to clarify the mechanism of formation of the biscubanes.

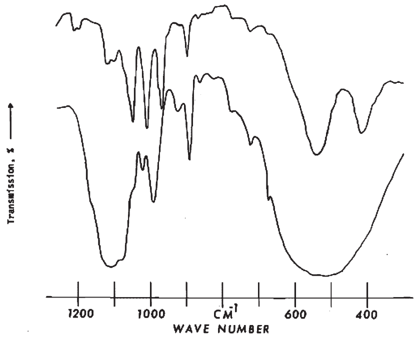

Figure 1. Infrared spectra of methylmagnesium *n*-propoxide, top, and its decomposition product when heated to 130 °C, bottom.

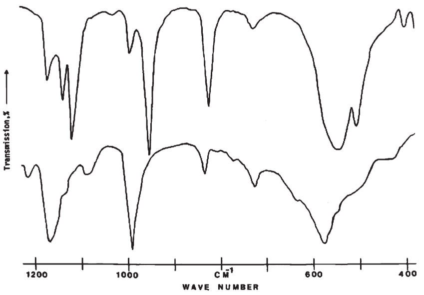

Figure 2. Infrared spectrum of methylmagnesium iso-propoxide, top, and its decomposition product when heated to 105 °C, bottom.

Unfortunately, Heitz et al.[1] did not report the IR spectra of their products. Thus, I am providing the IR spectra for the *n*-propoxide and iso-propoxide compounds as isolated and after thermal decomposition that were included in my 1974 thesis[4] but not in the publication[2] (Figures 1 and 2, respectively). These spectra may be useful to compare our observations from 1974 to recent work[1] and may help clarify the mechanism of formation of the biscubanes. Unfortunately, in 1974 we did not anticipate the importance of MgO in semiconductors or nanotechnology and made no attempt to investigate the decomposition products.

George E. Parris*
Tufts University School of Medicine, 9601 Warfield Road,
Gaithersburg, Maryland 20882

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