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Organometallic Access to Intermetallic θ-CuE_2 (E = Al, Ga) and $Cu_{1-x}Al_x$ Phases

Mirza Cokoja,[a] Balaji R. Jagirdar,[b] Harish Parala,[a] Alexander Birkner,[c] and Roland A. Fischer*[a]

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In this work, we compare different precursor approaches for the mild decomposition to copper–aluminum and –gallium powder materials in nonaqueous solution. Referring to previous work on the preparation of Cu–Al alloy materials from $[(AlCp^*)_4]$ and $[CpCu(PMe_3)]$, the amine-stabilized metal trihydrides $[(Me_3N)AlH_3]$ and $[(quinuclidine)GaH_3]$ were used as alternative sources for Al and Ga. In a comparative study, $[(Me_3N)AlH_3]$ and $[(AlCp^*)_4]$ were treated with the Cu precursors $[CpCu(PMe_3)]$ and $[\{Cu(mesityl)\}_5]$ in mesitylene solution in various molar ratios at 150 °C and 3 bar H_2 to give metallic precipitates of the composition $Cu_{1-x}Al_x$ (x = 0.67, 0.50, 0.31). Whereas the combination $[(AlCp^*)_4]$ with $[\{Cu(mesityl)\}_5]$ did not yield an intermetallic phase, all other Cu/Al precursor combinations led to alloyed Cu–Al materials. For x = 0.67, the θ-$CuAl_2$ phase formed, as shown by X-ray powder diffraction (XRD) and solid-state magic-angle-spinning (MAS)NMR spectroscopic studies. Similarly, the reaction of $[\{Cu(mesityl)\}_5]$ with $[(quinuclidine)GaH_3]$ immediately led to the precipitation of a gray powder, without the addition of hydrogen. The powder was identified by means of XRD as θ-$CuGa_2$. At x = 0.50 and below, the reactions were less phase selective depending on the precursor combination. $[CpCu(PMe_3)]$ combined with both Al precursors afforded a mixture of several Cu–Al phases, whereas $[\{Cu(mesityl)\}_5]$ was treated with $[(Me_3N)AlH_3]$ to yield a material whose X-ray signature was assigned to the monoclinic $Cu_{0.51}Al_{0.49}$ phase. The γ-Cu_9Al_4 phase could not be obtained from $[CpCu(PMe_3)]$; instead, solid solutions of α-Cu were obtained. The treatment of $[\{Cu(mesityl)\}_5]$ with $[(Me_3N)AlH_3]$ in the Cu/Al molar ratio of 9:4 (x = 0.31) gave a gray powder, which could be identified by XRD as γ-Cu_9Al_4.