

PT5 Is copper worth more than silver? Comparison of [MeMR]⁻ (where M = Cu and Ag) syntheses.

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The gas phase syntheses of [MeMR]⁻ (where M = Cu and Ag) are compared.

Whilst organocopper reagents are widely valued as reagents in organic synthesis, the same cannot be said for their organosilver analogues.[1] A double decarboxylation has been used to form organometallates, [RMR']⁻, from dicarboxylate anions, [RCO₂MO₂CR']⁻. Dimethylargenate anions [MeAgMe]⁻ can be generated in the gas phase [2] and exhibit different reactivity than dimethylcuprate anions [3]; and many mixed organocuprates [RCuR']⁻ can be formed.[4]

We extend this approach to the generation of mixed organoargenates [MeAgR]⁻. Multistage mass spectrometry was used to probe the fragmentation of dicarboxylates, [RCO₂AgO₂CR']⁻. A novel use of ¹³C labeling allows isomer distinction upon decarboxylation. [MeAgMe]⁻ and [MeAgR]⁻ (where R = Et, Pr, Allyl, Bn, Ph) could be formed, whereas [EtAgEt]⁻, and [MeAgR]⁻ (where R = ⁱPr, ^tBu) could not. Fragmenting differently, organoargenates were more difficult to form than related organocuprates, consistent with DFT calculations. Thus the perception of organometallic chemists that organosilver reagents are difficult to form and handle seems to be borne out by these fundamental gas phase studies.

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[3] P.F. James, R.A.J. O'Hair, Org. Lett. 2004, 6: 2761-2764.

[4] N. Rijs, G. N. Khairallah, T. Waters, R. A. J. O'Hair, J. Am. Chem. Soc. 2008, 130: 1069-1079.