

Note

Reversed-phase thin-layer chromatography of metallocarboranes

JEFFREY S. PLOTKIN and LARRY G. SNEDDON*

Laboratory for Research on the Structure of Matter and Department of Chemistry, University of Pennsylvania, Philadelphia, Pa. 19104 (U.S.A.)

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Out of the inorganic chemists' increased understanding of carborane and metallocarborane chemistry has come the ability to make cage compounds which differ structurally in only very subtle ways. Naturally, with the synthesis of these closely related compounds, has come the need for more sensitive separation techniques and as a result, the development of the new chromatographic techniques necessary for the separation of these compounds has paralleled the synthetic advancements. Thus column chromatography has given way to preparative thin-layer chromatography (TLC) and even high-pressure liquid chromatography (HPLC)¹. We now wish to report that the use of reversed-phase TLC, a technique which has been rarely used by organometallic chemists, is very effective in the separation of closely related metallocarboranes. We found that separations can be achieved, which are comparable to those obtained with reversed-phase HPLC but at a fraction of the cost. In addition, since the effectiveness of the separation can be monitored visually, the determination of the best solvent system is quickly and easily made with the aid of small analytical plates. As an illustration of this technique, we describe here a specific application of reversed-phase TLC to the separation of a series of metallocarboranes which were inseparable using other techniques.

EXPERIMENTAL

Preparative reversed-phase plates were made by impregnating 0.5 mm (20 × 20 cm) cellulose plates (Analtech MN 300F) with nujol by development in a 10% (w/w) nujol-benzene solution, followed by air drying in an efficient hood. Analytical plates (0.25 mm, 5 × 20 cm) were made in the same fashion. Samples were streaked as methylene chloride solutions, thoroughly dried, and developed in the same direction as the nujol coating was applied. The resulting bands were extracted with methylene chloride which also removed the nujol. The compounds were freed of nujol by washing with hexane on a short silica gel column.

RESULTS AND DISCUSSION

The recent discovery that the mercury sensitized photolysis of many boranes or carboranes at 2537 Å results in the production of the corresponding boron-boron

* To whom correspondence should be addressed.

bonded coupled borane or carborane in high yields²⁻³, has made it possible to exploit the chemistry of these multi-cage systems. In particular, it was found that the mercury sensitized photolysis of the small closo carborane, 2,4-C₂B₅H₇, yields an isomeric mixture containing six coupled compounds of the formula (2,4-C₂B₅H₆)₂. The thermal reaction of this isomeric mixture with (η-C₅H₅)Co(CO)₂ resulted in the formation of a complex mixture of new metallocarboranes⁴.

When this mixture of metallocarboranes was chromatographed on silica gel plates using carbon tetrachloride as the eluent, two distinct bands were isolated (*R_F* 0.66 and 0.58). These bands appeared to contain pure compounds since all attempts at further separation on silica gel plates using a variety of eluent mixtures were unsuccessful. The spectroscopic data obtained from the mass spectra, ¹¹B and ¹H nmr spectra indicated, however, that each band contained at least three different compounds and that six of the compounds had the general formula C₂B₅H₆-C₂B₅H₆Co₂(C₅H₅)₂. Reversed-phase TLC was then successfully used to separate these mixtures.

The most mobile band from the silica gel plates was chromatographed on reversed-phase plates in a methanol-water (94:6) eluent mixture and was separated into three compounds: 2-[1'-(2',4'-C₂B₅H₆)]-1,8,5,6-(η⁵-C₅H₅)₂Co₂C₂B₅H₆, *R_F* = 0.58, 2-[3'-(2',4'-C₂B₅H₆)]-1,8,5,6-(η⁵-C₅H₅)₂Co₂C₂B₅H₆, *R_F* = 0.49 and 2-[5'-(2',4'-C₂B₅H₆)]-1,8,5,6-(η⁵-C₅H₅)₂Co₂C₂B₅H₆, *R_F* = 0.44. The less mobile band from the silica gel plates was found to consist of four compounds when chromatographed on reversed-phase plates using a methanol-water (96:4) eluent mixture: the known 1,8,5,6-(η⁵-C₅H₅)₂Co₂C₂B₅H₇ (Ref. 5), *R_F* = 0.78 and the new compounds 3-[1'-(2',4'-C₂B₅H₆)]-1,8,5,6-(η⁵-C₅H₅)₂Co₂C₂B₅H₆, *R_F* = 0.69, 3-[3'-(2',4'-C₂B₅H₆)]-1,8,5,6-(η⁵-C₅H₅)₂Co₂C₂B₅H₆, *R_F* = 0.61, and 3-[5'-(2',4'-C₂B₅H₆)]-1,8,5,6-(η⁵-C₅H₅)₂Co₂C₂B₅H₆, *R_F* = 0.57.

The separation of these six new metallocarboranes, which differ only with respect to the sites of connection of the carborane and metallocarborane cages, clearly demonstrates the great sensitivity and usefulness of reversed-phase TLC when applied to metallocarborane chemistry. We have had similar success using this technique to separate a variety of other organometallic compounds, especially metallo-fluorocarbon complexes. Reversed-phase TLC, when utilized as a complimentary technique to "normal" phase thin-layer methods (*i.e.* polar stationary phase, non-polar mobile phase) has also been found to be a very effective means of routinely checking sample purity.

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REFERENCES

- 1 W. J. Evans and M. F. Hawthorne, *J. Chromatogr.*, 88 (1974) 187.
- 2 J. S. Plotkin and L. G. Sneddon, *Chem. Commun.*, (1976) 95.
- 3 J. S. Plotkin and L. G. Sneddon, in preparation.
- 4 J. S. Plotkin and L. G. Sneddon, in preparation.
- 5 V. R. Miller and R. N. Grimes, *J. Amer. Chem. Soc.*, 95 (1973) 2830.