Tetrahedron Letters,Vol.25,No.9,pp 899-900,1984
Printed in Great Britain
0040-4039/84 \$3.00 + .00

A GENERAL SYNTHESIS OF BIS(η^6-[2_n]CYCLOPHANE)RUTHENIUM(II) COMPOUNDS

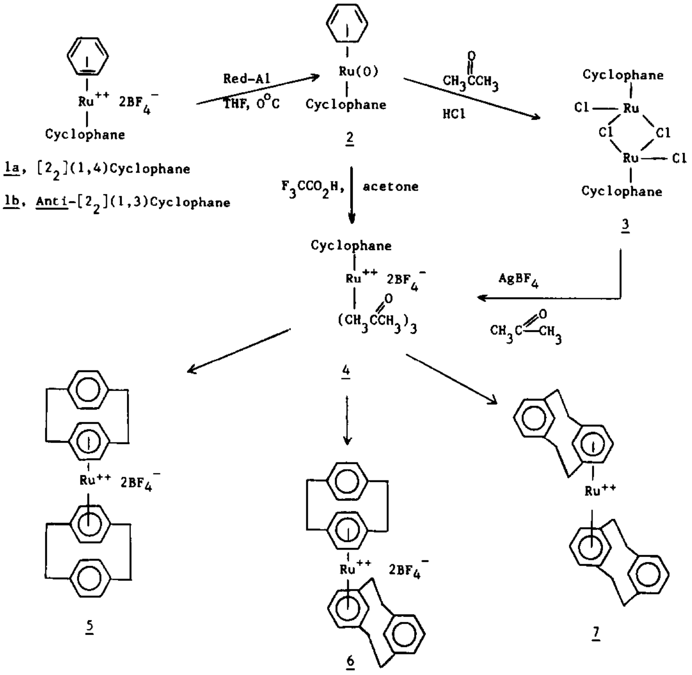
R. Thomas Swann and V. Boekelheide
Department of Chemistry, University of Oregon, Eugene, Oregon 97403

Abstract: Hydride reduction of (η^6-arene)(η^6-[2_n]cyclophane)ruthenium(II) compounds, followed by treatment with acid, gives (η^6-[2_n]cyclophane)ruthenium(II) solvates and thus provides a general synthesis for bis(η^6-[2_n]cyclophane)ruthenium(II) compounds.

The preparation of polymers of [2_n]cyclophane-metal complexes and studies of the intramolecular electron transmission properties of model subunits related to such polymers are of both practical and fundamental interest.[1-6] Until now studies of electron transmission properties have been hindered by a lack of good, general, synthetic methods for preparing suitable model compounds. Although syntheses of bis(η^6-[2_n]cyclophane)metal complexes, where the metal is chromium, iron, or ruthenium, have been reported,[5,6,8,9] these methods have been limited either in scale or in generality. We now present a good, general procedure for preparing bis(η^6-[2_n]-cyclophane)ruthenium(II) derivatives via ruthenium(0) intermediates.

We find that Red-Al reduction of (η^6-benzene)(η^6-[2_2](1,4)cyclophane)ruthenium(II), 1a, proceeds smoothly to give (η^4-1,3-cyclohexadiene)(η^6-[2_2](1,4)cyclophane)ruthenium(0), 2a, in 67% yield.[10] Treatment of 2a with a degassed solution of concentrated hydrochloric acid in acetone leads to the di-μ-chlororuthenium(II) species 3a in 96% yield. Reaction of 3a with silver tetrafluoroborate in acetone then generates the (η^6-[2_2](1,4)cyclophane)ruthenium(II) solvate 4a and this, in the presence of [2_2](1,4)cyclophane, gives bis(η^6-[2_2](1,4)cyclophane)ruthenium-(II) bis(tetrafluoroborate) (5) in 84% yield. Alternatively, treatment of 4a with *anti*-[2_2](1,3)-cyclophane leads to 6 in 82% yield. Repetition of the sequence starting with (η^6-benzene)(η^6-*anti*-[2_2](1,3)cyclophane)ruthenium(II) bis(tetrafluoroborate) (1b) results in the corresponding derivatives 2b, 3b, and 4b. Treatment of 4b with *anti*-[2_2](1,3)cyclophane then gives 7 in 82% yield.[15]

We have also found that treatment of the ruthenium(0) derivative 2 with a solution of trifluoroacetic acid in acetone leads directly in high yield to the ruthenium(II) solvate ion shown in 4. Aside from serving as a precursor for bis(η^6-[2_n]cyclophane)ruthenium(II) derivatives such as 5, 6, and 7, 4 is also a potential key intermediate for synthesizing oligomers and polymers. Thus, the experiments now described offer a basic, and general, method for preparing monomer units for a wide range of [2_n]cyclophane-metal complexes and, possibly, their corresponding polymers.



Acknowledgment This work was supported by the National Science Foundation, Grant CHE-8210282.

References and Notes

1. E. D. Laganis, R. G. Finke, and V. Boekelheide, Tetrahedron Lett., 21, 4405 (1980).
2. E. D. Laganis, R. G. Finke, and V. Boekelheide, Proc. Natl. Acad. Sci. USA, 78, 2657 (1981).
3. E. D. Laganis, R. H. Voegeli, R. T. Swann, R. G. Finke, H. Hopf, and V. Boekelheide, Organometallics, 1, 1415 (1982).
4. R. G. Finke, R. H. Voegeli, E. D. Laganis, and V. Boekelheide, Organometallics, 2, 347 (1983).
5. Ch. Elschenbroich, R. Möckel, and U. Zenneck, Angew. Chem., 90, 560 (1978); ibid, Angew. Chem., Int. Ed. Engl., 17, 531 (1978).
6. J. Elzinga and M. Rosenblum, Tetrahedron Lett., 23, 1535 (1982).
7. a) M. A. Bennett and T. W. Matheson, J. Organometal. Chem., 175, 87 (1979). b) M. A. Bennett, T. W. Matheson, G. B. Robertson, A. K. Smith, and P. Tucker, Inorg. Chem., 19, 1014 (1980).
8. W. D. Rohrbach and V. Boekelheide, J. Org. Chem., 48, 3673 (1983).
9. J. Elzinga and M. Rosenblum, Organometallics, 2, 1214 (1983).
10. a) For $[2_n]$cyclophane nomenclature, see V. Boekelheide, Topics Curr. Chem., 113, 87 (1983). b) Although other hydride reagents can be used, Red-Al $(NaAlH_2(OCH_2CH_2OCH_3)_2)$ has been the most satisfactory in our experience. c) For examples of other hydride reductions of ruthenium(II) complexes, see D. Jones, L. Pratt, and G. Wilkinson, J. Chem. Soc., 4458 (1962); S. L. Grundy and P. M. Maitlis, J. Chem. Soc., Chem. Commun., 379 (1982); and M. I. Rybinskaya, V. Kaganovich, and A. Kudinov, J. Organometal. Chem., 235, 215 (1982).
11. P. Pertici, G. Vitulli, R. Lazzaroni, and P. Salvadori, J. Chem. Soc., Dalton Trans., 1019 (1982).
12. All new compounds being reported have been fully characterized and their spectral properties and composition are in agreement with their assigned structures. 1b: colorless needles (prepared in good yield as previously described[1,3]), mp > 270°C dec; 2a: yellow solid (67%), mp 152-154°C; 3a: white solid (96%), mp > 250°C; 5a: yellow plates (84%), mp > 260°C dec; 6: yellow needles (82%), mp 264-265°C; 3b: red solid (71%), mp > 250°C dec; 7: white powder (97%), mp 265-266°C dec.

(Received in USA 12 December 1983)