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MULTILAYERED TRANSITION METAL COMPLEXES OF CYCLOPHANES

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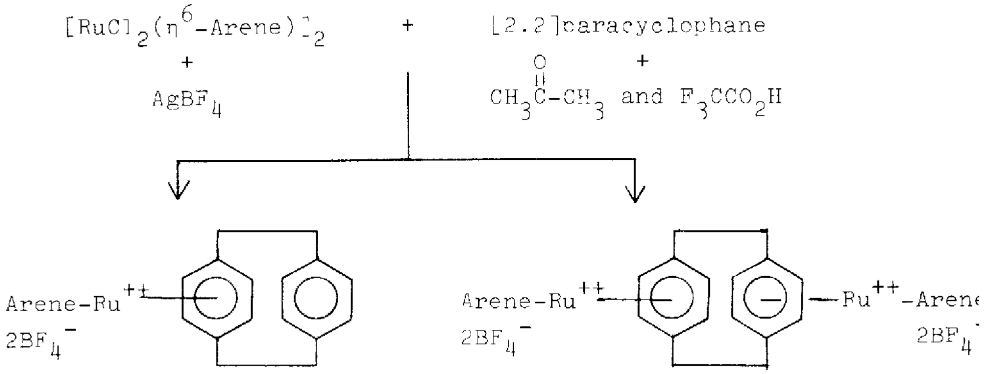
Summary: The reaction of arene-ruthenium complexes ($[RuCl_2(\eta^6\text{-arene})]_2$) with [2.2]paracyclophane in the presence of $AgBF_4$ provides double- and triple-layered arene-ruthenium complexes of [2.2]paracyclophane in excellent yield.

Although the properties of cyclophanes are consistent with the concep of a single Π-electron system for the whole molecule,[1,2] the possibility still exists for forming transition metal complexes at both aromatic faces of a cyclophane. This has long been of interest, since it would allow syntheses of oligomers and polymers having Π-electron systems extending over the whole of the macromolecular framework. We now report the realization of this goal of preparing multilayered transition metal complexes of cyclophanes.

Work directed toward this end in the past has been restricted essentially to two approaches: 1) the reaction of cyclophanes with hexacarbonylchromium, and 2) the reaction of cyclophanes with metal atoms. In the early study of Cram and Wilkinson, the reaction of [2.2]paracyclophane with hexacarbonylchromium gave only a mono-tricarbonylchromium complex,[3] and this is the common experience of others,[4,5] although Misumi and his colleagues, by using forcing conditions, were able to prepare the bis-tricarbonylchromium complex of [2.2]paracyclophane in poor yield.[6] Likewise, Elschenbroich has shown that the chromium metal-atom technique converts [2.2]paracyclophane to a mixture of bis(η^6-[2.2]paracyclophane)-chromium(0) and (η^{12}-[2.2]paracyclophane)chromium(0).[7] However, neither of these methods is suited for preparing oligomers and polymers of cyclophane-transition metal complexes.

With the completion of syntheses of all of the possible symmetrical $[2_n]$cyclophanes,[8] we wanted to compare the various cyclophanes with respect to their ability to form transition metal complexes and also to reexamine the possibility of preparing oligomers and polymers. Fortunately, at this time, Bennett and his colleagues described simple, convenient methods for preparing bis(arene)-ruthenium(II) complexes.[9,10] When we employed Bennett's procedure, substituting [2.2]paracyclophane for the second arene, formation of double- and triple-layered [2.2]paracyclophane-ruthenium complexes (1 and 2) occurred readily in excellent yield.



1 2

The following procedure for the preparation of 1 (Arene = p-cymene) is typical. Bis(p-cymene)dichlorodi-μ-chloro-diruthenium(II)[11] (104 mg, 0.12 mmol), silver tetrafluoroborate (104 mg, 0.536 mmol), and acetone (3 ml) were stirred at room temperature for 20 min. The precipitated silver chloride was removed by filtration before adding [2.2]paracyclophane (50 mg, 0.24 mmol) and trifluoroacetic acid to the yellow-orange solution. The resulting solution was boiled under reflux for 35 min, and ether was added. The white powdery solid (127 mg, 86%), which separated, was essentially pure. On recrystallization from 95% ethanol it gave pale yellow needles of 1 (Arene = p-cymene).[12] When this experiment was repeated using a five-fold excess of bis(p-cymene)dichlorodi-μ-chloro-diruthenium(II), triple-layered complex, 2 (Arene = p-cymene), was isolated in 53% yield.[12] The yield and ^1H NMR date for all of these cyclophane-transition metal complexes are presented in Table 1.

Table 1: Yield and ^{1}HNMR Data for Arene-Cyclophane Ruthenium Complexes.

	Yield(%)	^{1}HNMR (δ, in CD_3CN)[13]
Structure **1**		
Arene-		
benzene	97	2.99-3.49 (8H,m,$-C\underline{H}_2-$); 6.08 (4H,s,Ar'$\underline{H}$);[a] 6.56 (6H,s,Ar$\underline{H}$); 7.00 (4H,s,Ar'$\underline{H}$)
mesitylene	99	2.25 (9H,s,$-C\underline{H}_3$); 2.96-3.48 (8H,m,$-C\underline{H}_2-$); 5.99 (4H,s,Ar'$\underline{H}$); 6.49 (3H,s,Ar$\underline{H}$); 6.94 (4H,s,Ar'$\underline{H}$)
p-cymene	86	1.18 (6H,d,J=4.2Hz,$-CH(C\underline{H}_3)_2$); 2.27 (3H,s,$-C\underline{H}_3$); 2.73 (1H,sp,J=4.2Hz,$-C\underline{H}(CH_3)_2$); 2.95-3.53 (8H,m,$-C\underline{H}_2-$); 6.10 (4H,s,Ar'$\underline{H}$); 6.54 (4H,s,Ar$\underline{H}$); 6.98 (4H,s,Ar'$\underline{H}$)
hexamethylbenzene	92	2.34 (18H,s,$-C\underline{H}_3$), 2.93-3.44 (8H,m,$-C\underline{H}_2-$); 5.82 (4H,s,Ar'$\underline{H}$); 6.88 (4H,s,Ar'$\underline{H}$)
Structure **2**		
Arene-		
mesitylene	18[b]	2.32 (18H,s,$-C\underline{H}_3$); 3.46 (8H,s,$-C\underline{H}_2-$); 6.47 (8H,s,Ar'$\underline{H}$)
p-cymene	53	1.21 (12H,d,J=4.2Hz,$-CH(C\underline{H}_3)_2$); 2.33 (6H,s,$-C\underline{H}_3$); 2.81 (2H,sp,J=4.2Hz,$-C\underline{H}(CH_3)_2$); 3.44 (8H,s,$-C\underline{H}_2-$) 6.53 (8H,s,Ar'$\underline{H}$); 6.69 (8H,s,Ar$\underline{H}$)
hexamethylbenzene	87	2.38 (36H,s,$-C\underline{H}_3$); 3.36 (8H,s,$-CH_2-$); 6.20 (8H,s,Ar'$\underline{H}$)

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a) Ar=arene and Ar'=[2.2]paracyclophane

b) Although the yield of **2** (arene=mesitylene) is only 18%, the remainder of the [2.2]paracyclophane is accounted for by isolation of **1** (arene=mesitylene).

The method employed for the preparation of these ruthenium complexes appears to be general in nature and we are investigating syntheses of multilayered cyclophane-transition metal complexes, their oligomers, and polymers with various transition metals and various $[2_n]$cyclophanes.

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References

1) V. Boekelheide and W. Schmidt, Chem. Phys. Lett., 17, 410 (1972).

2) B. Kovac, M. Mohraz, E. Heilbronner, V. Boekelheide, and H. Hopf, J. Am. Chem. Soc., 102, 4314 (1980).

3) D. J. Cram and D. I. Wilkinson, J. Am. Chem. Soc., 82, 5721 (1960).

4) E. Langer and H. Lehner, Tetrahedron, 29, 375 (1973).

5) A. F. Mourad and H. Hopf, Tetrahedron Lett., 1209 (1979).

6) H. Ohno, H. Horita, T. Otsubo, Y. Sakata, and S. Misumi, Tetrahedron Lett., 265 (1977).

7) C. Elschenbroich, R. Mockel, and U. Zenneck, Angew. Chem., 90, 560 (1978); Angew. Chem. (Int. Ed. Eng.), 17, 531 (1978).

8) V. Boekelheide, Acc. Chem. Res., 13, 65 (1980).

9) M. A. Bennett and T. W. Matheson, J. Organometal. Chem., 175, 87 (1979).

10) M. A. Bennett, T. W. Matheson, G. B. Robertson, A. K. Smith, and P. A. Tucker, Inorg. Chem., 19, 1014 (1980). We thank Professor Bennett for providing us with a description of his method for preparing bis(hexamethylbenzene)dichloro-μ-chlorodiruthenium(II) prior to this publication.

11) M. A. Bennett and A. K. Smith, J.C.S., Dalton, 233 (1974).

12) The composition of all new compounds being reported is supported by satisfactory elemental analyses. Melting points are not given because all of these ruthenium complexes decomposed slowly over a wide temperature range when heated above 225°C in a sealed, evacuated melting point tube. The molecular weights of two of the complexes were determined by field desorption mass spectra: η^6-benzene-η^6-[2.2]paracyclophaneruthenium(II) bisfluoroborate, m/e, 385, 386, 387, and 388 (Calc. for the isotopes of $C_{22}H_{22}Ru^+$: 385, 386, 387, and 388); η^6-mesitylene-η^6-[2.2]paracyclophaneruthenium(II) bisfluoroborate, m/e, 427, 428, 429, and 430 (Calc. for the isotopes of $C_{25}H_{28}Ru^+$: 427, 428, 429, and 430). We thank Professor K. L. Rinehart for measuring these field desorption mass spectra.

13) For comparative purposes all of the ^{1}H NMR spectral data are given for solutions in CD_3CN. However, some of these solutions, on standing, show evidence of displacement of the arene ligands by CD_3CN. In other solvents, such as deuterium oxide and perdeuterionitromethane, this does not occur.

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