minimized was $\sum w(|F_o| - |F_c|)$ with the weight, $w$, assigned as $1/\sigma^2(F_o)$. The final discrepancy factors are $R_1 = 0.051$ and $R_2 = 0.051$. A final difference Fourier map was featureless with the highest residual electron equal to 0.25 e/Å$^3$. The final fractional coordinates are given in Table VII and the final values of the thermal parameters in the supplementary material.

**Acknowledgment.** The X-ray structure analysis was done in the Crystallographic Research Center, Osaka University. We are very grateful to Prof. N. Yasuoka of the Research Center for his valuable advice throughout the X-ray work and to Dr. W. E. Rhine of the University of Dayton Research Institute for suggestions regarding the manuscript.

**Registry No.** **7a**, 86238-29-1; **8a**, 86238-30-4; **8b**, 86238-31-5; **9a**, 86217-14-3; **9c**, 86217-17-6; **9d**, 86217-15-4; **9e**, 86238-32-6; **11a**, 86217-18-7; **12a**, 86217-16-5.

**Supplementary Material Available:** Tables of structure factors, anisotropic thermal parameters, and H atom parameters (with esd's), and deviations from the plane of the pentadiene or ruthenacyclic ring (18 pages). Ordering information is given on any current masthead page.

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# ([2.2]Paracyclophane)iron(II) Complexes. Synthesis and Intramolecular Charge-Transfer Interactions

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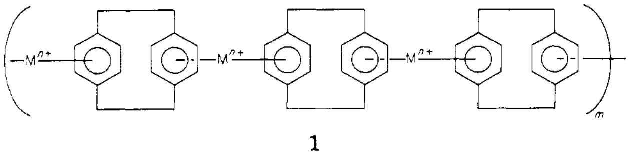
*Received March 15, 1983*

As part of a project designed to examine synthetic routes to organometallic polymers based on [2.2]paracyclophanes, a number of new bis(arene)iron(II) salts have been prepared from [2.2]paracyclophanes, employing a modification of the Fischer–Hafner synthesis. These include the parent complex 4 (M = $Fe^{2+}$), the bis(tetramethyl[2.2]paracyclophane)iron(II) bis(hexafluorophosphate) complexes **6** and **11b**, and the bis(octamethyl[2.2]paracyclophane)iron(II) bis(hexafluorophosphate) complex **11a**. The electronic spectra of **11a,b** in the region of 400–600 nm show significantly enhanced absorption compared with the spectrum of bis(hexamethylbenzene)iron bis(hexafluorophosphate). This is assigned to charge-transfer interactions between the complexed and noncomplexed aromatic rings in the paracyclophane complexes. An attempt to extend complexation in **11a** by treatment with tris(acetone)($p$-cymene)ruthenium(II) dication led to disruption of the arene–iron bond and the formation of the ($p$-cymene)([2.2]paracyclophane)ruthenium(II) salt **17**.

Although a number of bis(arene)iron(II) and ruthenium(II) complexes are known,[1] none derived from a paracyclophane had until recently been described.[2] Our interest in these substances and their transition-metal congeners derived from their possible use as monomeric components in the construction of multilayered or columnar organometallic polymers of general structure 1. Such polymers might be expected to exhibit unique properties of electrical conduction, since physical data,[3] chemical reactivity studies,[4] and theoretical analyses[5] all suggest extensive through space orbital interaction between the aromatic rings of [2.2]paracyclophane. The combination of such interactions and those associated with metal–ring bonding should provide a macromolecular framework with extensive orbital delocalization leading to band formation.



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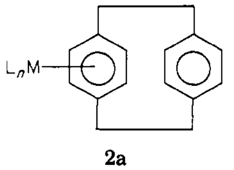
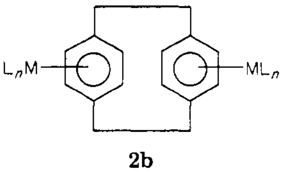
Of the three general classes of (paracyclophane)metal complexes 2, 3, and 4, those of type 4 seemed to us best suited for elaboration to oligomeric or polymeric structures such as 1. A number of complexes of structure 2[6] are known, and one of structure 3[7] has been reported, but none



2a



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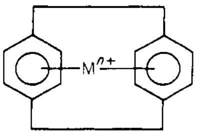

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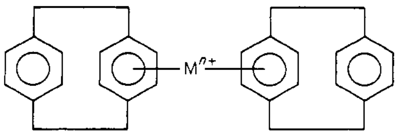

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[1] For a partial listing of these through 1968, see: "Organometallic Compounds", 2nd ed.; Dub, M. Ed.; Springer Verlag: New York, 1966, Vol. and first supplement, 1975.

[2] (a) Elzinga, J.; Rosenblum, M. *Tetrahedron Lett.* **1982**, 1535. (b) Laganis, E. D.; Finke, R. G.; Boekelheide, V. *Ibid.* **1980**, 4405. Laganis, E. D.; Finke, R. G.; Boekelheide, V. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 2657.

[3] For a review of these as well as chemical studies, see: Vögle, F.; Nuemann, P. *Top. Stereochem.* **1974**, *48*, 67.

[4] Cram, D. J.; Cram, J. M. *Acc. Chem. Res.* **1971**, *4*, 205.

[5] Kovac, B.; Mohraz, M.; Heilbronner, E.; Boekelheide, V.; Hopf, H. *J. Am. Chem. Soc.* **1980**, *102*, 4314.

[6] Cram, D. J.; Wilkenson, D. I. *J. Am. Chem. Soc.* **1960**, *82*, 5721. Langer, E.; Lehner, H. *Tetrahedron* **1973**, *29*, 375. Mourad, A. F.; Hopf, H. *Tetrahedron Lett.* **1979**, 1209. Ohno, H.; Horita, H.; Otsubo, T.; Sakata, Y.; Misumi, S. *Ibid.* **1977**, 265. Cristiani, F.; DeFilippo, D.; Deplano, P.; Devillanova, F.; Diaz, A.; Trogu, E. F.; Verani, G. *Inorg. Chim. Acta* **1975**, *12*, 119.

[7] Elschenbroich, C.; Möckel, R.; Zenneck, U. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 531.

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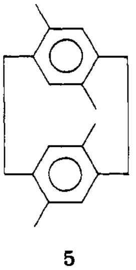
of form 4 had been isolated. We recently reported briefly the preparation of two members of this latter class of compound, the Fe(II) complexes of [2.2]paracyclophane and of 4,7,12,15-tetramethyl[2.2]paracyclophane. This paper provides a full account of this work, of the preparation and properties of more highly methylated (paracyclophane)iron complexes, and of preliminary attempts to extend complexation in one of these.

## Results and Discussion

Of the large number of bis(arene)metal complexes known,[8] encompassing almost all of the transition elements, the most general method employed for their synthesis has been that due to Fischer and Hafner[9] in which the arene is allowed to react with a transition metal halide in the presence of aluminum halide and aluminum powder. Since [2.2]paracyclophanes undergo rapid and irreversible acid-catalyzed isomerization in the presence of traces of $HAlCl_4$,[10] it is not surprising that the Fischer synthesis is inapplicable to the preparation of transition-metal complexes of this aromatic system. However, it has recently been shown[11] that alkylaluminum halides serve as effective catalysts in the ene reaction, since they both function as Lewis acid catalysts and, by reacting irreversibly with protons, prevent proton-initiated polymerization and isomerization of reactants. We have found that this technique is also applicable to the preparation of ([2.2]-paracyclophane)iron(II) cations.[12] These reactions are best run in refluxing heptane solution in the presence of $AlCl_3$ and of $Me_3Al_2Cl_3$ as proton scavenger. With [2.2]paracyclophane itself, the yield of product complex 4 ($M = Fe^{2+}$) after gegenion ion exchange with ammonium hexafluorophosphate, was low. Furthermore, the instability of the salt in nitromethane or acetonitrile solutions and even as a solid at room temperature made full characterization of this substance difficult. These observations prompted us to turn to the preparation of methylated analogues of 4, since it had earlier been observed by Tsutsui and Zeiss[13] that solvolytic stability of bis(arene)iron(II) salts are increased markedly by ring methylation.

The tetramethyl[2.2]paracyclophane 5 is readily prepared from durene, following the synthesis of Longone and Chow.[14] Treatment of this substance with ferrous chloride, aluminum chloride, and methylaluminum sesquichloride in refluxing cyclohexane gave the bis(tetramethyl[2.2]paracyclophane)iron complex 6, isolated as the hexafluorophosphate salt, in 78% yield. The orange-red complex was found to be stable in the air at room temperature and moderately stable in nitromethane solutions below 0 °C. Although the structure of complex 6 is shown with $D_2$ symmetry, it is not known if the product has this or $C_{2h}$ symmetry or is a mixture of two such isomers.



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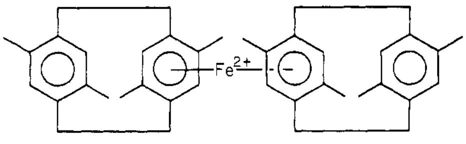

6

We were encouraged by these results to prepare the fully methylated analogus. A short synthesis of octamethyl-[2.2]paracyclophane 10a from pentamethylbenzyl bromide by the classical Hofmann elimination procedure was reported some time ago by Longone and Simanyi.[15] However, the product was obtained only in low yield and was reported to be unstable both in solution and as a solid. More recently this substance has been prepared by a rather long sequence of transformations from 4,5,12,13-tetracarbomethoxy[2.2]paracyclophane by Eltmany and Hopf.[16] The compound was described as high melting solid, entirely stable in this form and in solution. We have repeated the earlier synthesis and find that the product is identical with that reported by Eltmany and Hopf and is stable when pure. However, because of the very low yields of 10a obtained from either of these syntheses, neither seemed practicable for the preparation of suitable quantities of starting material. We have, however, found that 10a can be readily prepared on gram scale by an adaptation of the photochemical extrusion of sulfur from dialkyl sulfides, a reaction first devised by Corey and Block[17] and later adopted by Bruhin and Jenny[18] and by Boekelheide, Reingold, and Tuttle[19] for the preparation of cyclophanes. The requisite bis(sulfide) 9a is obtained in 23% yield by high dilution[20] condensation of 1,4-bis(chloromethyl)durene[21] (7a) with 1,4-bis(thiomethyl)durene (8), itself readily available in high yield from 7a or 7b.[22] The importance of inter-ring repulsions in retarding the formation of 9a is suggested by the observation that the condensation of 8 with 1,4-bis(thiomethyl)benzene gave the partially methylated bis(sulfide) 9b in substantially better yield (71%).

Irradiation of 9a in trimethyl phosphite solution gave only traces of octamethyl[2.2]paracyclophane 10a, owing in large measure to the instability of the product under conditions of prolonged irradiation, required because of the insolubility of the bis-sulfide in trimethyl phosphite. Furthermore, the need to hydrolyze this solvent to effectively remove it during workup made it unsuitable for larger scale preparations. However, irradiation of 9a,b can be much more effectively carried out in a mixture of benzene and methylene chloride, containing trimethyl phosphite. The bis(sulfides) 9a,b are more soluble in this medium, and photolysis, using a Hanovia 450-W medium-pressure UV lamp and a corex filter, is complete within an hour. Isolated yields of 10a and 10b[23] were 55 and 61%, respectively.

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[8] Silverthorn, W. E. *Adv. Organomet. Chem.* **1975**, *13*, 47. Dub, M. "Organometallic Compounds"; Springer-Verlag: New York, 1966; Vol. 1. Bauer, K.; Haller, G. "Organometallic Compounds"; Springer-Verlag, New York, 1975; Vol. 1.

[9] Fischer, E. O.; Hafner, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem. Biochem., Biophys., Biol.* **1955**, *B10*, 665.

[10] Cram, D. J.; Helgeson, R. C.; Lock, D.; Singer, L. A. *J. Am. Chem. Soc.* **1966**, *88*, 1324.

[11] Snider, B. B. *Acc. Chem. Res.* **1980**, *13*, 426.

[12] An earlier preparation of several bis(arene)chromium(I) complexes employing triethylaluminum and chromic chloride has been reported. Tsutsui, M.; Chang, G. *Can. J. Chem.* **1963**, 41, 1255.

[13] Zeiss, H. H.; Tsuisui, M. *Naturwissenschaften* **1957**, *44*, 420.

[14] Longone, D. T.; Chow, H. S. *J. Am. Chem. Soc.* **1970**, *92*, 994.

[15] Longone, D. T.; Simanyi, L. H. *J. Org. Chem.* **1964**, *29*, 3245.

[16] Eltamany, S. H.; Hopf, H. *Tetrahedron Lett.* **1980**, 4901.

[17] Corey, E. J.; Block, E. *J. Org. Chem.* **1969**, *34*, 1233.

[18] Brukin, J.; Jenny, W. *Tetrahedron Lett.* **1973**, 1215.

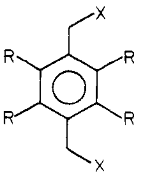
[19] Boekelheide, V.; Reingold, I. D.; Tuttle, M. *J. Chem. Soc., Chem. Commun.* **1973**, 406. Boekelheide, V. *Acc. Chem. Res.* **1980**, *13*, 65.

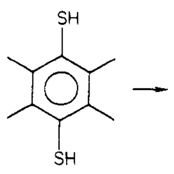
[20] A continuous dilution apparatus was employed. Davis, A. C. *Chem. Ind. (London)* **1977**, 203.

[21] Available from Aldrich Chemical Co., Milwaukee, WI. The procedure given in the Experimental Section represents an improvement of that previously reported for the preparation of this compound. Rhoad, M. J.; Flory, P. J. *J. Am. Chem. Soc.* **1950**, *72*, 2216.

[22] The use of the bromomethyl compound 7b affords lower yields of 9a. Similar observations have been made in the preparation of [2.2]paracyclophane through the corresponding bis(sulfide). Brink, M. *Synthesis* **1975**, 807.

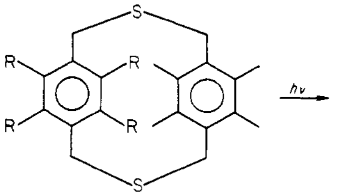
[23] Bruhin, J.; Gerson, F.; Ohya-Nishiguchi, H. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1045.



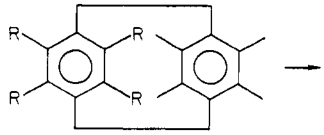


**7a–c** **8a–c**

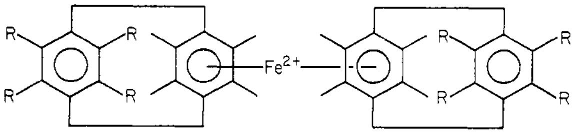
**a**, R = Me, X = Cl; **b**, R = Me, X = Br; **c**, R = H, X = Cl



**9a**, R = Me
**b**, R = H

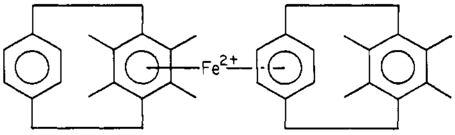


**10a,b**

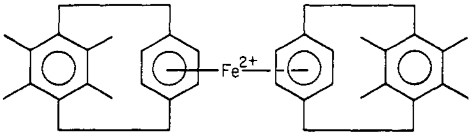


**11a,b**
**a**, R = Me; **b**, R = H

Iron(II) complexes of **10a,b** were prepared by using the modified Fischer and Bötcher[24] synthesis of bis(benzene)iron(II) salts, which we employed earlier in the synthesis of **4** (M = $Fe^{2+}$) and of **6**.[2a] Complex **11a**, obtained in 79% yield, as the hexafluorophosphate salt, is a dark red, air-stable solid. The complex decomposes at 105–110 °C, a temperature considerably lower than the decomposition temperature of bis(hexamethylbenzene)iron bis(hexafluorophosphate). This may reflect a weaker metal–ring bond, derived from the enforced nonplanarity of the benzene rings in the paracyclophane complex. The substance is nevertheless considerably more stable in nitromethane solution than is **6**. In this solvent its half-life at room temperature is about 2 h, while that of **6**, under these conditions, is less than 5 min. The increased solution stability of **11a** may be due to the screening action of the methyl substituents which retard solvolytic displacement of the arene rings.



**12**



**13**

When complexation of the unsymmetrical tetramethyl[2.2]paracyclophane **10b** was carried out, the product, obtained in 88% yield, could be shown by low-temperature (−20 °C) NMR studies to be a 1:1 mixture of two of the possible three isomeric complexes **11b** and **12**. The absence of **13** in the mixture of products is not surprising in view of the instability of **4** (M = $Fe^{2+}$), and indeed complex **12** decomposes rapidly at room temperature in nitromethane-$d_8$ liberating the free ligand **10b**. By contrast complex **11b** is somewhat more stable in nitromethane solution than **11a**, with a half-life of about 4 h at room temperature. It is not possible to separate **11b** from **12**, but, when the latter complex is allowed to decompose in solution, **11b** can be obtained free of its isomer. The structures assigned to the stable and labile complexes are supported by their proton NMR spectra and a comparison of these with spectral data for **10a,b** and **11a**. These data as well as that for complex **6**, bis(hexamethylbenzene)iron (**14**), and bis(durene)iron bis(hexafluorophosphate) (**15**) as well as the uncomplexed arenes are summarized in Table I.

In none of the complexation reactions was any oligomeric or polymeric organometallic product observed. Since the initially formed bis(paracyclophane)iron(II) salts are highly insoluble in the reaction medium and separate from solution in the course of reaction, it is possible that further complexation is precluded simply on this account. However, interannular electronic interaction, which would be expected to diminish the donor character of the uncomplexed rings in **6**, **11a**, or **11b**, are possibly more important.

The proton NMR spectral data in Table I provide little information on this point since the effect of the complexed ring on shielding of arene and methyl protons in the uncomplexed ring is very small (0–0.1 ppm).

A better measure of interannular electronic interaction in these complexes is provided by a comparison of the electronic absorption spectra of the paracyclophane complexes **11a** and **11b** with bis(hexamethylbenzene)iron bis(hexafluorophosphate) (**14**). Spectra for these three substances are shown in Figure 1. The absorption bands at 325, 456, and 534 nm in **14** have been assigned to spin-allowed d–d transitions, with the high extinction coefficient for the band at 325 nm attributed to intensity borrowing from $\pi$–$\pi^*$ excitations.[25] A striking feature in both the spectra of **11a** and **11b** compared with that of **14** is the considerably enhanced absorption of the paracyclophane complexes throughout the visible region. Furthermore, absorption is much greater between 400 and 600 nm for **11a**, and $\lambda_{max}$ is bathochromically shifted for this complex compared with **11b**. These changes would be difficult to account for in terms of perturbation of d–d transitions alone but are plausibly attributable to superposition of charge-transfer interactions between complexed and uncomplexed rings on the normal d–d transitions. Sufficient precedent for such interactions is at hand in the observation of Braitsch[26] that stable, colored charge-transfer complexes, involving bis(hexamethylbenzene)iron(II) (**14**) or bis(durene)iron(II) (**15**) salts and a number

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(24) Fischer, E. O.; Böttcher, R. *Chem. Ber.* **1956**, *89*, 2397. Fischer, E. O.; Rohrsheid, R. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1962**, *17*, 483. Helling, J. F.; Braitsch, D. M. *J. Am. Chem. Soc.* **1970**, *92*, 7207.

(25) Morrison, W. H.; Ho, E. Y.; Hendrickson, D. N. *Inorg. Chem.* **1975**, *14*, 500.

(26) Braitsch, D. M. *J. Chem. Soc., Chem. Commun.* **1974**, 460. Although it appears likely that complex formation does occur between 14 or 15 and some donor aromatic molecules, e.g., *p*-phenylenediamine, the reported complex of 14 with ferrocene is *not* a charge-transfer complex. The structure of this substance consists of discrete bis(hexamethylbenzene)iron(II) cations and ferrocene molecules, well separated by interleaving $PF_6^-$ anions. (Foxman, B. M.; Howland, D. S., unpublished observations). We thank Professor Foxman for communicating these results to us.

Table I. Proton Chemical Shifts for Arenes and $(Arene)_2Fe(PF_6)_2$ Complexes

| compound | chemical shift,[a] δ | | | |
|---|---|---|---|---|
| | ring protons | | ring methyl protons | |
| durene | | 6.87[c] | | 2.17[c] |
| $(durene)_2Fe(PF_6)_2$ (**15**) | 6.51[b] | | 2.59[b] | |
| hexamethylbenzene | | | | 2.20[c] |
| $(hexamethylbenzene)_2Fe(PF_6)_2$ (**14**) | | | 2.45[b] | |
| **5** | | 6.42[c] | | 2.00[c] |
| **6** | 6.15[b] | 6.55[c] | 2.30[b] | 2.05[c] |
| **10b** | | 6.62[c] | | 1.92[c] |
| **11b** | | 6.73[c] | 2.30[b] | |
| **12** | 5.78[b] | 6.73[c] | 2.40[b] | 1.92[c] |
| **10a** | | | | 2.06[c] |
| **11a** | | | 2.42[b] | 2.06[c] |

[a] From internal $Me_4Si$, taken in $CD_3NO_2$ solution. [b] Complexed. [c] Noncomplexed.

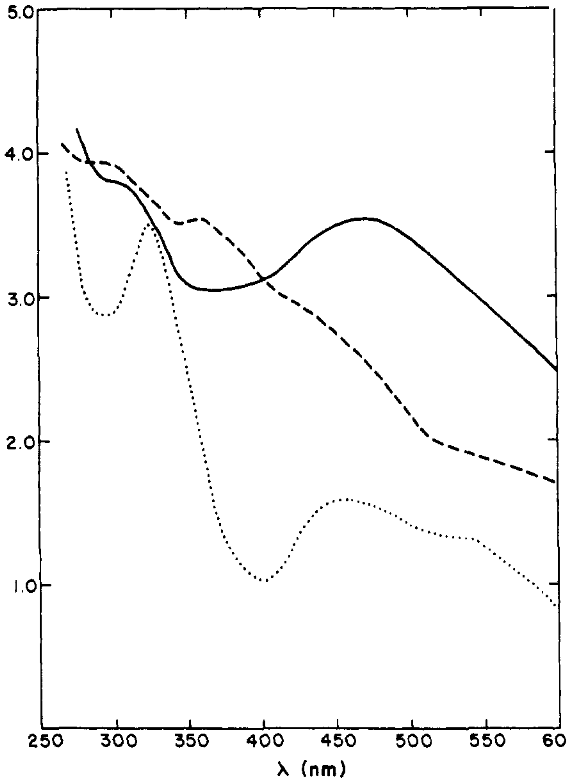
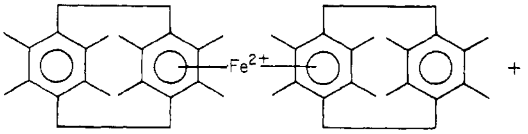


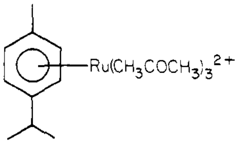
**Figure 1.** Spectra were determined in acetonitrile solution: bis(hexamethylbenzene)iron bis(hexafluorophosphate) (**14**), ···; bis(tetramethyl[2.2]paracyclophane)iron bis(hexafluorophosphate) (**11b**), - - -; bis(octamethyl[2.2]paracyclophane)iron bis(hexafluorophosphate) (**11a**), —.

of aromatic compounds may be isolated from acetone solutions on mixing these components. Donor–acceptor interactions have also been observed between paracyclophane rings in [2.2](1,4)tropyliocyclophane[27] and in quinhydrone type [2.2]paracyclophanes.[28]

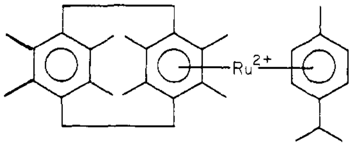
Finally, we attempted to extend the complexation in **11a** by treatment with tris(acetone)(p-cymene)ruthenium(II) dication **16**, following the procedure of Bennett and Matheson[29] for the synthesis of mixed bis(arene)ruthenium(II) dication. These reactions, even under comparatively mild conditions, which led to the recovery of some starting material, gave the ruthenium complex **17** as the only product.



**11a**

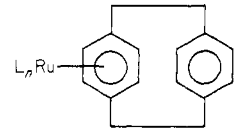


**16**

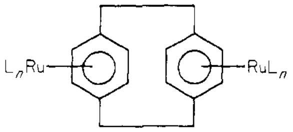


**17**

These results stand in contrast to those of Laganis, Finke, and Boekelheide,[2b] who recently reported the preparation of singly and doubly complexed [2.2]paracyclophanes **18** and **19**, employing the synthetic approach of Bennett and Matheson.[29]



**18**



**19**

The formation of **19** probably reflects the stronger metal–arene bond in the ruthenium complexes and suggests that if a mixed ruthenium, iron complex is formed in the reaction of **11a** and **16**, it may well be thermodynamically unstable as a consequence of charge-transfer interactions across the paracyclophane ring and the poor back-bonding ability of $Fe^{2+}$ compared with $Ru^{2+}$.[30]

It seems likely then that, although relatively stable $Fe^{2+}$ complexes of paracyclophanes can be prepared, extended complexation with this metal is unlikely. A further examination of other transition metals more suited to the purpose of preparing organometallic polymers based on complexation of [2.2]paracyclophane is being pursued.

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[27] O'Connor, J. G.; Keehn, P. M. *J. Am. Chem. Soc.* **1976**, *98*, 8446.

[28] Staab, H. A.; Rebafka, W. *Chem. Ber.* **1977**, *110*, 3333.

[29] Bennett, M. A.; Matheson, T. W. *J. Organomet. Chem.* **1979**, *175*, 87. See also: Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233.

[30] Domaille, P. J.; Ittel, S. D.; Jesson, J. P., Sweigart, D. A. *J. Organomet. Chem.* **1980**, *202*, 191.

## Experimental Section

Solvents were routinely dried by standard procedures and stored under nitrogen.

All organometallic reactions and subsequent manipulations including reagent additions, filtrations, extractions, recrystallizations, and chromatographies as well as the preparation of NMR samples and solution IR samples were conducted under a nitrogen atmosphere.

Infrared spectra were recorded on Perkin-Elmer spectrophotometers, Models 137 and 457. $^1$H nuclear magnetic resonance spectra were recorded on the following spectrometers: Perkin-Elmer R-32 (NSF GU 3852), Bruker WH-90 (NSF GU 3852, GP 37156), and Varian EM 390 and Bruker WH-90 (NSF GU 3852, GP 37156). Mass spectra were determined with an AEI MS-12 direct inlet spectrometer (NSF GP-3644). Ultraviolet and visible spectra were obtained with a Perkin-Elmer Model 323 spectrophotometer.

Melting points were determined under a nitrogen atmosphere on a Kofler hot stage equipped with a polarizing microscope and are uncorrected.

Elemental analyses were determined by Microlytics, S. Deerfield, MA.

**(Bis[2.2]paracyclophane)iron Bis(hexafluorophosphate) (4).** To a stirred mixture of 900 mg (7.5 mmol) of ferrous chloride[31] and 900 mg (7.0 mmol) of aluminum chloride in 500 mL of hexane under nitrogen was added by syringe 3 mL of a heptane solution of trimethylaluminum trichloride (1.5 mmol). After the mixture was refluxed for 30 min, 205 mg (1.0 mmol) of paracyclophane was added portionwise. The mixture soon turned red in color, and a red-brown precipitate appeared. Refluxing was continued for 1 h, then the mixture was cooled to 0 °C, and a few drops of 2-propanol were added by syringe, followed by methanol and then ice. Stirring was continued for 15 min until the red-brown solid had dissolved. The brilliant orange aqueous layer was separated, washed twice with 20 mL of cold hexane, and then filtered. Rapid addition of a cold aqueous solution of ammonium hexafluorophosphate to the filtrate gave an orange precipitate, which was collected by centrifugation, washed with cold water, and dried in vacuo to give 100 mg (26%) of 4 (M = Fe) as an orange powder. All manipulations in aqueous solution must be done rapidly since the salt is easily hydrolyzed. The complex salt is insoluble in hexane and ether and slightly soluble in acetone but dissolves readily in nitromethane or acetonitrile to give orange-red solutions which bleach rapidly (1 m at 25 °C) due to decomposition. The salt is also unstable as a solid at room temperature but may be stored at −20 °C.

**Decomposition of (Bis[2.2]paracyclophane)iron Bis(hexafluorophosphate).** A freshly prepared sample of 4 (M = Fe) (35 mg, 0.046 mmol), washed with ether to remove traces of free paracyclophane, was heated to 150 °C in vacuo in a small sublimation apparatus. The orange powder turned off-white, and 20 mg of sublimate (0.096 mmol), shown by melting point and mixed melting point to be paracyclophane, was collected.

**Bis(4,7,12,15-tetramethyl[2.2]paracyclophane)iron Bis(hexafluorophosphate) (6).** To a stirred mixture of 500 mg (4.0 mmol) of $FeCl_2$,[31] 500 mg (3.0 mmol) of $AlCl_3$, and 25 mL of cyclohexane under nitrogen was added by syringe 4 mL of a heptane solution of $Me_3Al_2Cl_3$ (2.0 mmol). After the mixture was refluxed for 2 h, 260 mg (1.0 mmol) of tetramethyl[2.2]paracyclophane[14] was added in small portions. The mixture turned reddish, and a red-brown precipitate formed. Boiling was continued for an additional hour, and the solution was then cooled to 0 °C and worked up as in previous experiments. The product 6 (350 mg, 78%) was obtained as an orange powder: mp 120–130 °C dec; $^1$H NMR ($CD_3NO_2$, −10 °C) $\delta$ 6.55 (s, 4 H, ArH), 6.15 (s, 4 H, ArH), 3.3–2.5 (m, 16 H, $CH_2$), 2.30 (s, 12 H, $CH_3$), 2.05 (s, 12 H, $CH_3$). Anal. Calcd for $C_{40}H_{48}FeP_2F_{12}$: C, 54.93; H, 5.53; Fe, 6.39. Found: C, 55.79; H, 5.95; Fe, 7.2.

**Bis(chloromethyl)durene (7a).** To a stirred mixture of 50 g (0.37 mol) of durene, 50 g (1.7 mol) of paraformaldehyde, 120 g (2.0 mol) of sodium chloride, and 300 mL of glacial acetic acid, heated at 90 °C, was added dropwise a mixture of 200 mL of concentrated sulfuric acid and 200 mL of glacial acetic acid. Reaction was continued at 90 °C for 1 h after addition, and after being cooled to room temperature, the mixture was poured onto 1 L of ice. The white precipitate was collected and washed several times with water until the washings were neutral. After being dried in vacuo, the product, mp 190–192 °C (lit.[21] 193–194 °C), weighed 83.0 g (97%).

Bis(bromomethyl)durene can be prepared in 95% following the above procedure and is obtained as a colorless solid, mp 212–213 °C (lit.[32] 214.5–215 °C).

**1,4-Bis(thiomethyl)durene (8).** To a stirred suspension of 47.0 g (0.145 mol) of bis(bromomethyl)durene in 200 mL of ethanol was added dropwise a solution of 38 g (0.50 mol) of thiourea in 250 mL of warm water, over a period of 1 h. After the addition was complete, the mixture was refluxed for 1 h, during which time a white precipitate formed. After the mixture was cooled to room temperature, a solution of 56 g (1.0 mol) of potassium hydroxide in 200 mL of water was added and the mixture was again refluxed for 2 h, during which time the precipitate dissolved. The yellow-brown solution was cooled to room temperature and filtered. The filtrate was then acidified with concentrated HCl. The off-white precipitate, which formed, was collected, was washed several times with water until the washings were neutral, and was finally dried in air to give 32.2 g (98%) of product. An analytical sample was obtained as colorless needles, mp 148–149 °C, by recrystallization from hexane: $^1$H NMR ($CDCl_3$) $\delta$ 3.77 (d, 4 H, $J$ = 7 Hz, $CH_2S$) 2.32 (s, 12 H, $CH_3$), 1.53 (t, 2 H, $J$ = 4 Hz, SH); MS, $m/e$ 226 ($M^+$). Anal. Calcd for $C_{12}H_{18}S_2$: C, 63.66; H, 8.01; S, 28.32. Found: C, 63.50; H, 8.16; S, 28.41.

**2,11-Dithia-5,6,8,9,14,15,17,18-octamethyl[3.3]paracyclophane (9a).** A solution of 6.9 g (30.0 mmol) of bis(chloromethyl)durene and 6.8 g (30.0 mmol) of bis(thiomethyl)durene in 450 mL of benzene was added dropwise[20] to a stirred, refluxing solution of 5.0 g (90.0 mmol) of potassium hydroxide in 1.5 L of alcohol. After addition was complete (60 h), refluxing was continued for an additional hour and the solution was then allowed to cool to room temperature. The white precipitate, which had formed, was collected, washed with ethanol, and dried in the air. Solvent was removed from the combined filtrate, leaving a white solid. This was extracted with 300 mL of methylene chloride, and the solution was then used for the Soxhlet extraction (2 days) of the initial white precipitate. After removal of solvent in vacuo, a white solid was obtained which contains 65% of the desired product, by NMR spectrometry, in addition to oligomers and polymers. Purification was achieved by column chromatography on alumina eluting with hexane–methylene chloride (1:1), to give 2.65 g (23%) of product. An analytical sample, mp 330–335 °C dec, was obtained by slow evaporation of a chloroform solution: $^1$H NMR ($CDCl_3$) $\delta$ 4.02 (s, 8 H, $CH_2S$), 2.23 (s, 24 H, $CH_3$); MS, $m/e$ 384 ($M^+$). This compound may also be obtained in 11% yield by using bis(bromomethyl)durene instead of the corresponding dichloro derivative.

Column chromatography of the crude disulfide product is rather tedious, owing to the low solubility of the substance. However, the crude unchromatographed product can be carried through to the next step without complication. Anal. Calcd for $C_{24}H_{32}S_2$: C, 74.94; H, 8.39; S, 16.67. Found: C, 74.74; H, 8.55; S, 16.72.

**4,5,7,8,12,13,15,16-Octamethyl[2.2]paracyclophane (10a).** A stirred, degassed suspension of 1.20 g (3.12 mmol) of the disulfide **9a** in a mixture of 300 mL of benzene, 50 mL of methylene chloride, and 50 mL of trimethyl phosphite was irradiated for 11 h with a 450-W medium-pressure Hanovia UV lamp, using a Corex filter sleeve. The mixture was then poured onto 100 g of crushed ice and stirred overnight. The two layers are separated, and the organic layer was washed with water and dried over magnesium sulfate. Solvent was removed in vacuo, and the residue was chromatographed on neutral alumina eluting with hexane, to give 550 mg (55%) of octamethyl[2.2]paracyclophane as a white solid. Further purification may be achieved by sublimation at 150–190 °C (0.01 mm), to give **10a** as colorless crystals: mp 275–277 °C (lit.[16] 273–275 °C); $^1$H NMR ($CDCl_3$) $\delta$ 3.20 (s, 8 H, $CH_2$), 2.08 (s, 24 H, $CH_3$); MS, $m/e$ 320 ($M^+$); UV max ($CH_2Cl_2$) 309 nm ($\epsilon$ 400).

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[31] Purchased from Alfa-Ventron Co., Danvers, MA 01923.

[32] Hoffman, J. A. U.S. Pat. 3917560; *Chem. Abstr.* **1976**, *84*, 45385e.

When the reaction was run in methylene chloride alone in the presence of trimethyl phosphite, all of the bis(sulfide) was consumed within 45 min and the yield of isolated product was 40%.

**2,11-Dithia-5,6,8,9-tetramethyl[3.3]paracyclophane (9b).** A solution of 5.25 g (30 mmol) of 1,4-bis(chloromethyl)benzene and 6.8 (30 mmol) of bis(thiomethyl)durene in 400 mL of benzene was added dropwise[20] to a stirred refluxing solution of 4.9 g (90 mmol) of potassium hydroxide in 1.5 L of alcohol. When the addition was complete (60 h), the mixture was refluxed for an additional hour. After being cooled to room temperature, the mixture was concentrated in vacuo to dryness and the residue was extracted thoroughly with methylene chloride. The combined extracts were filtered, and solvent was removed in vacuo to leave a faintly yellow solid residue. Column chromatography on alumina with hexane–methylene chloride (1:1) afforded 7.01 g (71%) of **9b** as a white solid. An analytical sample, obtained by slow evaporation of a chloroform solution, gave the product as colorless rectangular crystals: mp 199–200 °C; $^1$H NMR ($CDCl_3$) $\delta$ 6.99 (s, 4 H, ArH), 3.94 (s, 4 H, $CH_2S$), 3.77 (s, 4 H, $CH_2S$), 2.18 (s, 12 H, $CH_3$); MS, *m/e* 328 ($M^+$). Anal. Calcd for $C_{20}H_{24}S_2$: C, 73.12; H, 7.36; S, 19.52. Found: C, 72.47; H, 7.16; S, 19.52.

**4,5,7,8-Tetramethyl[2.2]paracyclophane (10b).** A stirred, degassed suspension of 2.00 g (6.1 mmol) of disulfide **7b** in 300 mL of benzene, 50 mL of methylene chloride, and 50 mL of trimethyl phosphite was irradiated for 1.5 h with a 450-W medium-pressure Hanovia UV lamp using a Corex filter sleeve. The mixture was then poured on an excess of crushed ice and stirred overnight. The two layers were separated, and the organic layer was washed with water and then dried over magnesium sulfate. Concentration of the solution left a slightly yellowish oil. This was chromatographed on alumina with hexane to give 1.02 g (63%) of **10b** as a colorless solid. An analytical sample, obtained by sublimation at 120–160 °C (0.01 mm), had a melting point of 107–108 °C: $^1$H NMR ($CDCl_3$) $\delta$ 6.57 (s, 4 H, ArH), 3.2–2.8 (m, 8 H, $CH_2$), 1.97 (s, 12 H, $CH_3$); MS, *m/e* 264 ($M^+$); UV max ($CH_2Cl_2$) 285 (sh) nm ($\epsilon$ 460) 309 (220). Anal. Calcd for $C_{20}H_{24}$: C, 90.85; H, 9.15. Found: C, 90.51; H, 9.51.

**Bis(4,5,7,8,12,13,15,16-octamethyl[2.2]paracyclophane)iron Bis(hexafluorophosphate) (11a).** To a stirred mixture of 250 mg (2.0 mmol) of ferrous chloride[31] and 260 mg (2.0 mmol) of aluminum chloride in 30 mL of hexane was added by syringe 8 mL of a solution of trimethyldialuminum trichloride[31] (4.0 mmol) in heptane, under a dry nitrogen atmosphere. The mixture was refluxed for 3 h, and then 160 mg (0.50 mmol) of octamethylparacyclophane was added in protions as a solid. The mixture slowly turned red and in the course of the reaction a red precipitate formed. Refluxing was continued for 2 h, and then the reaction was cooled to −78 °C and 1 mL of 2-propanol followed by 2 mL of methanol were introduced by syringe to destroy excess trimethylaluminum trichloride. After the mixture was warmed to room temperature, crushed ice was added and the mixture was stirred for 20 min, while the mixture is kept cold by external cooling in an ice bath. When all the precipitate had dissolved, the mixture was transferred to a separatory funnel and the brilliant red aqueous solution was separated, washed with ether, and filtered. A solution of 1 g of ammonium hexafluorophosphate in 5 mL of water was added to the cold filtrate, and the red precipitate which resulted was collected by centrifugation and washed several times with cold water, then with cold methanol, and finally with ether. After being dried in vacuo, the product (195 mg, 79%) was obtained as a dark red powder. the salt can be obtained as dark red crystals, mp 105–110 °C dec (sealed tube), by diffusion recrystallization with nitromethane–ether at −20 °C: $^1$H NMR ($CD_3NO_2$) $\delta$ 3.1 (br m, 16, $CH_2$), 2.42 (s, 24, $CH_3$), 2.06 (s, 24, $CH_3$). Anal. Calcd for $C_{48}H_{64}FeP_2F_{12}$: C, 58.38; H, 6.54. Found: C, 57.58; H, 6.68.

**Bis(4,5,7,8-tetramethyl[2.2]paracyclophane)iron Bis(hexafluorophosphate) (11b).** A stirred mixture of 250 mg (2.0 mmol) of ferrous chloride,[31] 280 mg (2.1 mmol) of aluminum chloride, and 6 mL of a heptane solution of trimethyldialuminum trichloride[31] in 20 mL of hexane was refluxed for 3 h in a nitrogen atmosphere. Tetramethyl[2.2]paracyclophane (130 mg, 0.50 mmol) was added portionwise as a solid. The mixture slowly turned dark brown, and a dark brown precipitate formed. Refluxing was continued for 2 h, and then the mixture was cooled to −78 °C and 1 mL of 2-propanol followed by 2 mL of methanol was added. After the mixture was warmed to 0 °C, ice was added and stirring was continued for 15 min at which time the precipitate had dissolved. The brown aqueous layer was separated, washed with ether, and filtered. A solution of 1 g of ammonium hexafluorophosphate in 5 mL of water was added to the cold filtrate to give a brown precipitate. This was collected by centrifugation, washed with cold water, a few milliliters of cold methanol, and finally ether. After being dried in vacuo, 190 mg (88%) of product was obtained as a 1:1 mixture of **11b** and **12**, as shown by its NMR spectrum ($CD_3NO_2$, −20 °C). Complex **11b** may be obtained as an orange powder by dissolving the mixture in nitromethane at room temperature, filtering the solution, and reprecipitating with ether. The product was washed with methanol and then ether. Anal. Calcd for $C_{40}H_{48}FeP_2F_{12}$: C, 54.93; H, 5.53; Fe, 6.39. Found: C, 55.02; H, 5.61; Fe, 6.02.

**Attempted Complexation of 11a with (*p*-Cymene)ruthenium(II).** To a stirred solution of 100 mg (0.16 mmol) of (*p*-cymene)ruthenium dichloride dimer in 5 mL of acetone was added 100 mg (0.51 mmol) of silver tetrafluoroborate. Precipitated silver chloride was filtered off, and the filtrate was concentrated to leave an orange oil, which was then dissolved in 3 mL of trifluoroacetic acid. Treatment of this with 23 mg (0.023 mmol) of **11a** at room temperature for 10 min and then with ether gave a brown precipitate which was collected by centrifugation (10 mg). An NMR spectral comparison shows this product to be identical with complex **17** prepared from (*p*-cymene)ruthenium(II) and **10a** (see below).

When the above reaction of (*p*-cymene)ruthenium(II) and **11a** was carried out at 0 °C for 10 min, mixtures of **11a** and **17** were obtained.

**(4,5,7,8,12,13,15,16-Octamethyl[2.2]paracyclophane)(*p*-cymene)ruthenium Bis(tetrafluoroborate) (17).** To a stirred solution of 70 mg (0.11 mmol) of (*p*-cymene)ruthenium dichloride dimer in 3 mL of acetone was added 90 mg (0.46 mmol) of silver tetrafluoroborate. After 15 min, silver chloride was filtered off and the solvent was removed in vacuo leaving an orange oil. This was dissolved in 3 mL of trifluoroacetic acid, and 30 mg (0.094 mmol) of **10a** was added. The solution turned dark brown. After the mixture was stirred at room temperature for 4 h, 10 mL of ether was added and the brownish precipitate was collected and washed with ether. Drying in vacuo left the poduct as an off-white powder (45 mg, 66%). Further purification was achieved by recrystallization from ethanol to give the product as pale yellow needles: $^1$H NMR ($CD_3NO_2$) $\delta$ 6.31 (s, 4, Ar), 3.5 (m, 8, $CH_2$), 2.50 (s, 12, $CH_3$), 2.34 (s, 3, $CH_3$), 2.20 (s, 12, $CH_3$), 1.28 (d, 6, $J$ = 7 Hz, $CH_3$).

When the reaction is carried out in the presence of a fourfold molar excess of (*p*-cymene)ruthenium chloride dimer, under the same reaction conditions, complex **17** is obtained in 85% isolated yield. Anal. Calcd for $C_{34}H_{46}B_2F_8Ru$: C, 55.99; H, 6.36. Found: C, 55.19; H, 6.52.

**Acknowledgment** is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

**Registry No.** 4, 82764-58-7; **6**, 82783-19-5; **7a**, 3022-16-0; **7b**, 35168-64-0; 8, 10519-84-3; **9a**, 85883-15-4; **9b**, 85883-16-5; **10a**, 77897-20-2; **10b**, 65304-59-8; **11a**, 85883-10-9; **11b**, 85883-12-1; **17**, 85883-14-3.