Syntheses of [2$_2$](1,4)Cyclophane-Ruthenium(II) Complexes via the Mono-Birch Reduction Product of 4,5,7,8-Tetramethyl[2$_2$](1,4)cyclophane

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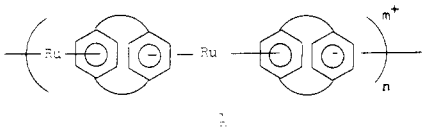
Convenient syntheses for 4,5,7,8-tetramethyl[2$_2$](1,4)cyclophane (**5**) and its mono-Birch reduction product (**6**) are described. By application of the Bennett procedure for converting dihydroarenes to arene-ruthenium(II) complexes, **6** has been converted to (η^6-4,5,7,8-tetramethyl[2$_2$](1,4)cyclophane) (**13**) and to bis(η^6-4,5,7,8-tetramethyl[2$_2$](1,4)cyclophane)ruthenium(II) bis(tetrafluoroborate) (**14**). These are the first syntheses of [2$_n$]-cyclophane-ruthenium-[2$_n$]cyclophane complexes and represent the first convenient method for making such cyclophane-metal complexes. The possible extension of this method to provide oligomers and polymers containing cyclophane-ruthenium(II) monomer units is complicated by the occurrence of ligand exchange.

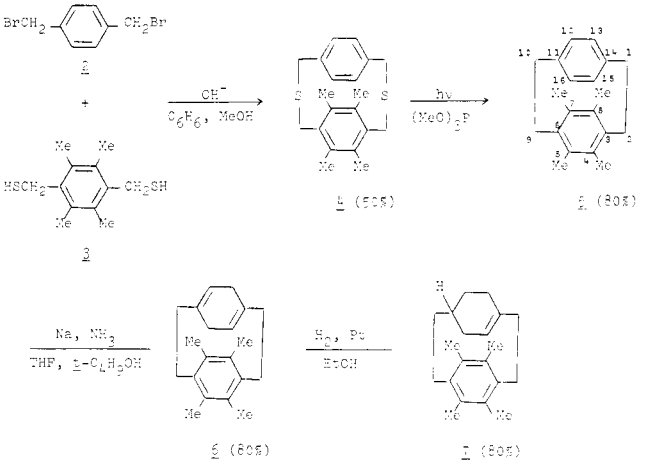
The construction of a polymer with monomer units of [2$_n$]cyclophane-transition metal complexes, as in **1**, is of



both theoretical and potential practical interest.[1-4] Although the preparation of chromium,[5-9] iron,[3,10-12] and ruthenium[2,4] complexes of [2$_n$]cyclophanes has been reported, there is at present no practical way of making [2$_n$]cyclophane-metal-[2$_n$]cyclophane complexes in reasonable quantity. We now describe a successful procedure for preparing such ruthenium complexes.

The general method of making ruthenium complexes of arenes is that devised by Bennett and his colleagues.[13,14]

Scheme I



As the first step in their procedure, a dihydroarene is heated in ethanol with ruthenium trichloride to give the corresponding bis(arene)dichlorodi(μ-chloro)diruthenium(II) derivative. Commonly, the precursor dihydroarenes are prepared by a Birch reduction of the arene. For our purpose, then, we needed a mono-Birch reduction product of a [2$_n$]cyclophane. Unfortunately, such mono-Birch reduction products of [2$_n$]cyclophanes are exceedingly rare.[15-20] Under Birch conditions reduction of both arene decks occurs even in the presence of excess [2$_n$]cyclophane. Although no mechanistic studies on the Birch reduction of [2$_n$]cyclophanes have been reported, the known experimental results suggest that the mono-Birch reduction product is not an intermediate and that the double-Birch reduction of [2$_n$]cyclophanes is probably another example of [2$_n$]cyclophanes behaving as a single delocalized π-electron system.

In several instances the isolation of mono-Birch reduction products of [2$_n$]cyclophanes have been reported.[21-23] However, the yields were low, and the possibility exists that these products resulted from partial aromatization of the double-Birch reduction products. In fact, Jenny and Reiner have reported that the double-Birch reduction product of [2$_2$](1,4)cyclophane undergoes thermal elimination of hydrogen to give the corresponding mono-Birch reduction product.[22] Even though this route involving

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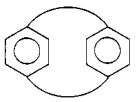

designates the general class of [2$_n$]cyclophanes. See: Boekelheide, V. *Top. Curr. Chem.* **1983**, *113*, 89.

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(23) Sekine, Y.; Boekelheide, V. *J. Am. Chem. Soc.* **1981**, *103*, 1777.

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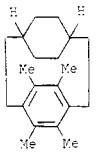
thermal elimination of hydrogen would appear to provide a convenient access to the mono-Birch reduction product of [2$_2$](1,4)cyclophane, our attempts to employ this procedure on a preparative scale were unsuccessful.

In view of the fact that hexamethylbenzene does not undergo Birch reduction, it occurred to us that a [2$_n$]-cyclophane completely substituted in one deck might undergo Birch reduction only in the less substituted deck and so provide a useful route to a mono-Birch reduction product of a [2$_n$]cyclophane. The molecule chosen for testing this hypothesis was 4,5,7,8-tetramethyl[2$_2$](1,4)-cyclophane (**5**), and its synthesis is presented in Scheme I. Although **5** and its tetradeuterio analogue have been reported previously,[24,25] our detailed procedure described in the Experimental Section provides improvements allowing for the preparation of **5** in quantity.

Under the usual conditions the Birch reduction of **5** proceeded smoothly to give the desired dihydro derivative **6** in 80% yield. The dihydro derivative **6**, when stored under nitrogen at low temperature, is stable indefinitely. However, when **6** is allowed to stand at room temperature, it slowly aromatizes to give back the precursor cyclophane **5**.

As yet, no [2$_n$]cyclophane having one deck saturated and the other deck aromatic has been prepared. The possibility of reducing **6** further to provide such an example was explored. Catalytic hydrogenation of **6** over platinum readily yielded the corresponding tetrahydro derivative **7** in 80% yield. However, attempts to effect a further reduction to **8**, either by catalytic hydrogenation or by reaction with diborane, were unsuccessful.

Examination of molecular models shows that a molecule such as **8** would embody an enormous amount of strain.



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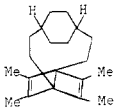

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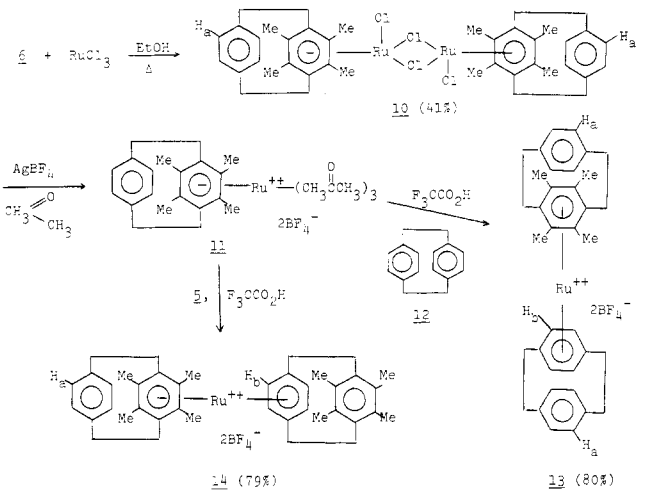
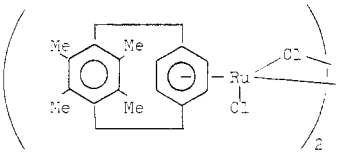
This was discussed previously by Cram and Allinger in describing their unsuccessful attempts to prepare the unsubstituted analogue of **8**.[26] One possible avenue for **8** to undergo relief of strain would be its conversion to the Dewar structure **9**. Jones, Bickelhaupt, et al. have previously reported that [6]paracyclophane does indeed undergo such a conversion to a Dewar benzene.[27] Thus, it seemed possible that a forced reduction of **7** might eventually yield **9**. However, this was not realized.

When 12,15-dihydro-4,5,7,8-tetramethyl[2$_2$](1,4)-cyclophane (**6**) was heated with ruthenium trichloride in ethanol, it gave a dimeric chloride (**10**) of the appropriate composition. Treatment of **10** with silver tetrafluoroborate in acetone then gave a ruthenium(II) solvate (**11**), and this, when warmed with [2$_2$](1,4)cyclophane (**12**), in the presence of trifluoroacetic acid, led to a [2$_n$]cyclophane–ruthenium(II)–[2$_n$]cyclophane complex (**13**). Alternatively, reaction of the solvate **11** with **5** in the presence of trifluoroacetic acid gave the corresponding complex **14**. Formation of each of the complexes, **13** and **14**, occurs in high yield. These syntheses, as presented in Scheme II, provide for the first time a convenient method for preparing stable [2$_n$]cyclophane–metal–[2$_n$]cyclophane complexes in useful quantities.

Scheme II



The assignment of structure for compounds **10**, **13**, and **14**, as given in Scheme II, has been made on the basis of ^{1}H and ^{13}C NMR spectral analyses, but this was not a trivial problem to solve. First of all, NMR spectral information on metal complexes of [2$_n$]cyclophanes is rather sparse, being limited to the tricarbonylchromium complexes of [2$_2$](1,4)cyclophane,[8,28] [2$_2$](1,3)cyclophane,[27] and [2$_2$](1,3)(1,4)cyclophane[28] and the iron complex of [2$_2$]-(1,3)cyclophane.[10] These data show that, with the tricarbonylchromium and iron complexes, the signal for the aromatic protons of the complexed deck of the cyclophane are shifted upfield, whereas the aromatic protons of the unbound deck are shifted downfield. A priori one would expect a similar behavior for ruthenium complexes. When **6** was heated with ruthenium trichloride in ethanol, it was also expected that the product would have structure **15**.



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However, the product isolated showed a signal at δ 7.01, representing a downfield shift of 0.43 ppm compared to that of the free cyclophane **5**.

It was clear, therefore, that either (a) the extrapolation of NMR behavior from the other metals, chromium and iron, to ruthenium was not warranted or (b) the ruthenium trichloride reaction with **6** had not followed the expected course. Previous studies of π-arene–metal complexes have shown that ^{13}C NMR spectra are much more sensitive to metal complexation than ^{1}H NMR spectra.[29,30] The ^{13}C NMR spectra of complexed arene rings show sizable upfield shifts compared to the free arenes. This effect, combined with the use of the proton-coupled ^{13}C NMR spectra to pinpoint which signal corresponded to which carbon, made a ^{13}C NMR spectral study an attractive way to settle the structural problem. Table I presents the ^{1}H and ^{13}C NMR data for the precursor cyclophane **5** and its various ruthenium complexes.

From the spectral data in Table I, it is clear the structure of the (η^6-4,5,7,8-tetramethyl[2$_2$](1,4)cyclophane)(η^6-

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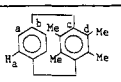
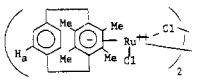
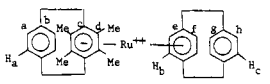
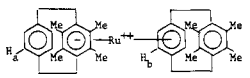
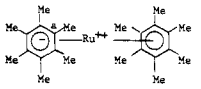
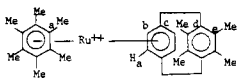
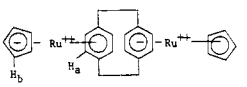
(30) Chisholm, M. H.; Godleski, S. *Prog. Inorg. Chem.* **1976**, *20*, 299.

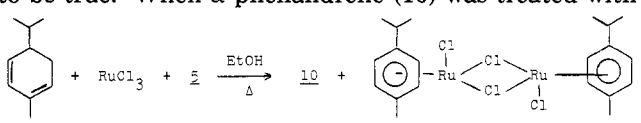
Table I. Cyclophane-Ruthenium(II) Complexes Comparison of Aromatic ^1H and ^{13}C NMR Chemical Shift Values

compd	structure	chemical shifts, δ ^1H	chemical shifts, δ ^{13}C
5		H_a 6.58	C_a 127.1 (d) (J = 157 Hz) C_b, C_c 139.0 (s), 136.4 (s) C_d 133.0 (s)
10		H_a 7.01	
13		H_a, H_c 6.91, 6.99 H_b 5.80	C_a, C_h 131.1 (J = 158 Hz), 135.6 (J = 162 Hz) C_b, C_g 140.1 (s), 141.3 (s) C_c, C_e 132.4 (s), 133.9 (s) C_d 100.2 (s) C_f 88.7 (J = 181 Hz)
14		H_a 6.99 H_b 5.80	
23			C_a 107.9 (s)
24		H_a 5.93	C_a 109.2 (s) C_b 88.2 (J = 182 Hz) C_c 131.3 (s) C_d, C_e 137.3 (s)
27		H_a 5.86 H_b 5.29	

[2_2](1,4)cyclophane)ruthenium(II) is correctly written as **13**. This is required both by the ^1H chemical shifts and their integrated areas as well as by the combination of ^{13}C signals and their pattern of proton coupling. The sharp, upfield shift of the metal-bound, aromatic carbon, C_f, of 39.5 ppm with a J_{C-H} = 182 Hz is particularly noteworthy. Reasoning back from structure **13** one can conclude that the structure of the ruthenium chloride dimer is **10**, and not **15**. Likewise, the cyclophane–ruthenium(II) solvate must have structure **11**.

The anomalous behavior therefore is in the reaction of **6** with ruthenium trichloride. Although the mechanism of the reaction of dihydroarenes with ruthenium trichloride to form arene–ruthenium(II) complexes is not known, the formation of **10** from **6** is surprising. In view of the ready electron transmission occurring between decks in [2_n]-cyclophanes, it was a conceivable, but unprecedented, possibility that approach of ruthenium(III) to the tetramethyl-substituted deck of **6** leads directly to **10** via an oxidation–reduction (electron transfer) process. On the other hand, a more prosaic possibility was that ruthenium(II) can undergo ligand exchange leading to **10** as the thermodynamically more stable product.

If ligand exchange were the important factor in the formation of **10**, one would expect that the reaction of other dihydroarenes with ruthenium trichloride in the presence of **5** would also produce **10**. In fact, this proved to be true. When α-phellandrene (**16**) was treated with



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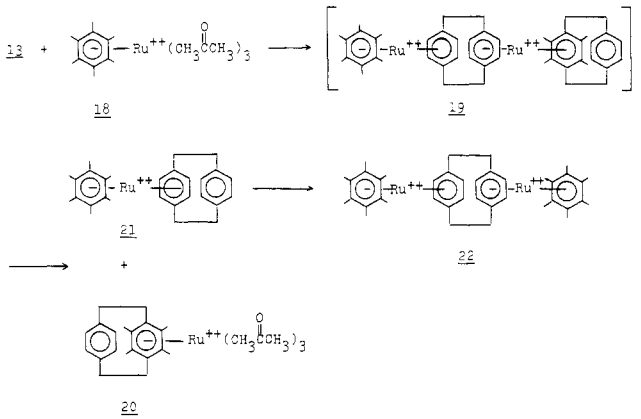
ruthenium trichloride in the presence of **5**, a mixture of the two dimeric chlorides, **10** and **17**, resulted. Control experiments showed that **5** alone does not react with ruthenium trichloride under these conditions, nor does **5** react with the dimeric chloride **17** on being heated in ethanol. Apparently, some other ruthenium species formed during the reaction of ruthenium trichloride with dihydroarenes in ethanol is responsible for the formation of **10** from **5**. Unfortunately, the mixture of dimeric chlorides, **10** and **17**, formed in the reaction with α-phellandrene (**16**) is difficult to separate, and this is not a practical method for preparing **10**.

As indicated earlier, our primary interest in the dimeric chloride **10** and its corresponding solvate **11** lay in their potential as precursors for preparing oligomers and polymers of [2_n]cyclophane–ruthenium complexes, as shown by **1**. When the acetone solvate **11** was heated alone in an acetone–trifluoroacetic acid solution, a complicated mixture of products resulted, suggesting the formation of oligomers, but isolation of pure, individual components was not successful.

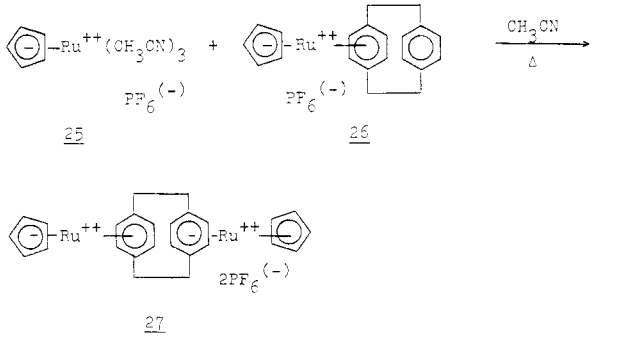
Treatment of **13** with (η^6-hexamethylbenzene)ruthenium(II) solvate (**18**) in the presence of trifluoroacetic acid was attempted in the hope of capping each of the "free" decks of **13** with a hexamethylbenzeneruthenium(II) moiety. However, the primary constituent of the resulting mixture was bis(η^6-hexamethylbenzene)(η^{12}-[2_2](1,4)-cyclophane)ruthenium(II) tetrakis(tetrafluoroborate) (**22**). Presumably, the first step occurred as desired to give **19**, but this underwent ligand solvolysis to give **20** and **21**. Subsequent capping of **21** could then lead to the observed product **22**.[4] Clearly, ligand exchange is a significant hurdle to be overcome in designing controlled syntheses of oligomers and polymers of [2_n]cyclophane–metal complexes. Alternate ways of accomplishing this are being explored.



To gain insight regarding the electron configuration of [2$_n$]cyclophane–ruthenium(II) complexes we have undertaken a study of their electrochemical behavior.[4] Cyclic voltammetry of **13** shows two separate reduction waves which, by coulometry, are of one electron each. The first wave occurs at $E_{1/2}$ = –0.63 V (i_a/i_c, 100 mV/s, 0.98) and the second at –0.77 V (i_a/i_c, 100 mV/s, irreversible) (vs. SCE). By comparison, bis(η^6-hexamethylbenzene)ruthenium(II) (compound **23**, Table I) shows a single, two-electron wave at –1.02 V (i_a/i_c, 100 mV/s, 0.36), and (η^6-hexamethylbenzene)(η^6-[2$_2$](1,4)cyclophane)ruthenium(II) (**21**) also shows a two-electron wave at –0.69 V (i_a/i_c, 100 mV/s, 0.94). Why **13** exhibits two separate, one-electron reduction waves whereas the obvious reference compounds **21** and **23** both show two-electron waves is not clear.

Another curiosity is the fact that reaction of **6** with ruthenium trichloride leads to the solvate **11**, where the ruthenium ion is complexed to the substituted deck of **5**, but reaction of the solvate **11** with **5** yields **14**, in which the ruthenium ion has complexed with the unsubstituted deck of **5**. This, of course, could be a result of thermodynamic control during the formation of **11** and kinetic control in the formation of **14**. To explore the question of whether in general the capping of metal ions occurs preferentially at the unsubstituted deck of **5** we allowed the (η^6-hexamethylbenzene)ruthenium(II) solvate (**18**) to react with **5**. A single product was isolated in 94% yield whose ^{1}H and ^{13}C NMR spectral data, as given in Table I, clearly show it to have structure **24** in which complexation of **5** has occurred at the unsubstituted deck.

Gill and Mann have recently described a photochemical method for preparing the (η^5-cyclopentadienyl)ruthenium(II) trisacetonitrile solvate (**25**) and have used this



reagent to prepare (η^5-cyclopentadienyl)(η^6-[2$_2$](1,4)-cyclophane)ruthenium hexafluorophosphate (**26**).[31] It seemed probable that the more electronegative cyclopentadienyl moiety would be less likely to undergo ligand exchange, and so Gill and Mann's reagent might be superior for capping cyclophanes. In fact, when a mixture of **26** and excess **25** was heated in acetonitrile, the desired doubly capped product **27** readily formed.

In view of the ease with which Gill and Mann's reagent provides capping, we also heated a mixture of **25** and **13** in acetonitrile in the hope of obtaining the corresponding oligomer complex having three ruthenium ions. Unfortunately, though, ligand exchange again occurred, giving a mixture of products of which **27** was the main constituent.

Experimental Section[32]

1,4-Bis(mercaptomethyl)durene (3). This was prepared as described in the literature.[33] To a boiling solution of 13.5 g (0.18 mol) of thiourea in 350 mL of ethanol stirred in a Morton flask was added 20.44 g (0.99 mol) of 1,4-bis(chloromethyl)durene over a 15-min period. After the boiling solution had been stirred for an additional 1.5 h, the solvent was removed under reduced pressure and a solution of 193 g (2.93 mol) of potassium hydroxide (85%) in 1 L of water was added. The mixture was heated 2 h on a steam bath before being neutralized by addition with stirring of a 50% aqueous sulfuric acid solution. Extraction of the mixture with chloroform followed by washing of the chloroform extract with water, drying, and concentration gave 17.9 g (90%) of white crystals, mp 153–154 °C (lit.[33] mp 150–152 °C).

2,11-Dithia-5,6,8,9-tetramethyl[3$_2$](1,4)cyclophane (4). To a solution of 10 g (0.18 mol) of potassium hydroxide (85%) and 150 mL of water in 3365 mL of methanol in a Morton flask was added dropwise with stirring a solution of 9.75 g (43 mmol) of dimercaptan (**3**) and 11.38 g (43 mmol) of 1,4-bis(bromomethyl)benzene (**2**) in 1120 mL of degassed benzene from a Hershberg funnel over a 3-day period. After removal of the solvent, the residue was extracted with a chloroform–water mixture. The chloroform extract was dried and concentrated. The crude residue was treated with a small amount of chloroform and the resulting mixture filtered to remove polymer. The filtrate was concentrated and the residue was chromatographed over neutral alumina (activity 1) with a 3:1 mixture of chloroform and hexane as eluent. From the main fraction of eluate there was isolated 7.1 g (50%) of a white powder. Sublimation of a sample of the powder gave white powdery crystals; mp 254 °C; IR (KBr) ν_{max} 2890, 1410, 1360 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.00 (4 H, s, Ar H), 3.96 (4 H, s, CH_2), 3.80 (4 H, s, CH_2), 2.19 (12 H, s, Ar CH_3).

Anal. Calcd for $C_{20}H_{24}S_2$: C, 73.12; H, 7.36. Found: C, 72.94; H, 7.44.

4,5,7,8-Tetramethyl[2$_2$](1,4)cyclophane (5). A solution of 1.10 g (3.35 mmol) of dithiacyclophane **4** in 380 mL of carefully degassed trimethyl phosphite was placed in a photochemical apparatus (400-W Hanovia lamp, quartz cooling jacket, immersion well, and Pyrex filter) and irradiated for 4 h while a slow stream of oxygen-free nitrogen was passed through the solution to effect stirring. After concentration of the solution to remove most of the trimethyl phosphite, the oily residue was hydrolyzed by boiling under reflux with 18% aqueous hydrochloric acid. The aqueous solution was then extracted with chloroform and the chloroform extract was washed with water, dried, and concentrated. The resulting residue was chromatographed over neutral alumina (activity 1) with a 4:1 hexane–chloroform mixture for elution. The

(31) Gill, T. P.; Mann, K. R. *Organometallics* **1982**, *1*, 485.

(32) The ^{1}H NMR spectra were determined with either Varian XL-100 (100 MHz) or Nicolet NT-360 (360 MHz) spectrometers. The ^{13}C NMR spectra were determined with a Nicolet NT-360 (90.7 MHz) spectrometer. Mass spectra were obtained with a CEC-21B-110 instrument set at 70 eV. Ultraviolet and visible spectra were measured with a Cary 15 spectrophotometer. Infrared spectra were taken with a Sargent Welch 3-200 infrared spectrometer. Melting points were determined using a Mel-Temp apparatus and are uncorrected. Elemental analyses are by Dr. R. Wielesek of the University of Oregon Microanalytical Laboratories. Preparative thin-layer chromatography was performed on precoated silica gel plates (1000 μm) supplied by Analtech. Tetrahydrofuran was distilled from sodium and benzophenone ketyl. Other solvents were reagent grade. The electrochemical measurements were made in the same manner as described previously.[4]

(33) (a) Du Vernet, R. G. Ph.D. Thesis, University of Oregon, Eugene, OR, 1974, p 145. (b) Martin, R. F.; Condo, F. E. U.S. Patent 2 986 582, May 30, 1961; Chem. Abstr. **1961**, *55*, 22921b.

main eluate fraction provided 710 mg (80%) of white crystals; mp 114 °C; IR (KBr) ν_{max} 940, 880, 790, 720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.58 (4 H, s, Ar H), 2.98 (8 H, m, CH_2), 1.95 (12 H, s, Ar CH_3); UV (CH_2Cl_2) λ_{max} 305 nm (ϵ 349); mass spectrum, m/e 264, 160; Anal. mol. weight calcd for $C_{20}H_{24}$, 264.188; found, 264.187 (high-resolution mass spectrum).

12,15-Dihydro-4,5,7,8-tetramethyl[2₂](1,4)cyclophane (6). To a stirred solution of 180 mg (7.8 mmol) of sodium in 100 mL of anhydrous ammonia held at −78 °C there was injected a solution 625 mg (2.4 mmol) of cyclophane **5** and 2.5 mL (26.5 mmol) of dry *tert*-butyl alcohol in 80 mL of tetrahydrofuran. After 20 min, the reaction mixture was quenched by addition of 6 mL of water, allowed to warm to room temperature, and then left to stand overnight. The residual liquid was extracted with dichloromethane and the dichloromethane extract was washed with water, dried, and concentrated. This gave 510 mg (80%) of **6** as a white, waxy solid. For further purification a sample of **6** was subjected to reverse-phase, high-pressure liquid chromatography on a Waters Associates C_{18}-Bondapak preparative column with acetonitrile as eluent. This gave a white solid; mp 95 °C; IR (KBr) ν_{max} 1380, 930, 865, 720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.96–4.88 (2 H, m = =CH), 3.02 (4 H, m, CH_2), 2.52–1.64 (8 H, m, CH_2), 2.14 (12 H, s, ArCH_3); UV (CH_2Cl_2) λ_{max} 297 nm (ϵ 363); mass spectrum, m/e 266, 160.

Anal. Calcd for $C_{20}H_{26}$: C, 90.16; H, 9.84. Found: C, 90.45; H, 9.46.

12,13,14,15-Tetrahydro-4,5,7,8-tetramethyl[2₂](1,4)-cyclophane (7). A solution of 100 mg (3.76 mmol) of **6** in 200 mL of absolute ethanol was subjected to hydrogenation over Adams catalyst (PtO_2) under 50 psi pressure of hydrogen for 2 h. After removal of the catalyst and solvent, the residual solid was purified by thin layer chromatography over silica gel to give 80 mg (80%) of a white, waxy solid; mp 101–103 °C; ^{1}H NMR ($CDCl_3$) δ 4.41–4.48 (1 H, m, =CH), 3.10–2.20 (4 H, m, CH_2), 2.20 (6 H, br s, Ar CH_3), 2.18 (6 H, br s, Ar CH_3), 1.96–1.32 (11 H, m); mass spectrum, m/e 268, 253.

Anal. Calcd for $C_{20}H_{28}$: C, 89.49; H, 10.51. Found: C, 89.03; H, 10.77.

Attempted Further Reduction of 7. A solution of 30 mg of **7** in 50 mL of absolute ethanol was subjected to hydrogenation over Adams catalyst (PtO_2) under 55 psi of hydrogen for 19 h. After removal of the catalyst followed by concentration, the residual solid was examined by thin layer chromatography over silica gel. The main component, and the only one to be identified, was recovered **7**. In addition there was evident from the chromatograms at least seven other substances, but these were present in too small a quantity to warrant further investigation.

To a solution of 67 mg of **7** in 4 mL of tetrahydrofuran was added 3.5 mL of a 1 M solution of diborane in tetrahydrofuran. After the solution had been stirred for 7 h, an additional 4 mL of the 1 M diborane solution was added and stirring was continued for another 5 h. Then, 7 mL of acetic acid was added and the solution was stirred vigorously for 0.5 h. The solution was neutralized by addition of an aqueous solution of sodium hydroxide and extracted with dichloromethane. Concentration of the dichloromethane extract followed by chromatography over silica gel gave a hydrocarbon fraction that consisted solely of recovered **7**.

Bis(η^6-4,5,7,8-tetramethyl[2₂](1,4)cyclophane)dichloro-(di-μ-chloro)diruthenium(II) (10). A mixture of 210 mg (0.79 mmol) of **6** and 20 mg (0.082 mmol) of ruthenium trichloride hydrate in 5 mL of absolute alcohol was boiled under reflux overnight. A black precipitate was removed by filtration and the filtrate was diluted with ether. The resulting precipitate was collected by filtration and washed with ether to give 14.7 mg (41%) of a burgundy-colored solid; mp dec >300 °C; IR (KBr) ν_{max} 2920, 1380, 795 cm^{-1}; ^{1}H NMR (Me_2SO-d_6), δ 7.01 (4 H, s, Ar H), 3.22–2.72 (8 H, AA′BB′, CH_2), 1.95 (12 H, s, Ar CH_3).

Anal. Calcd for $C_{40}H_{48}Ru_2Cl_4$: C, 55.05; H, 5.54. Found: C, 54.18; H, 4.98.

Formation of 10 via α-Phellandrene Oxidation. A mixture of 16.3 mg (0.67 mmol) of ruthenium trichloride hydrate, 232.0 mg (0.88 mmol) of **5**, and 48.2 mg (0.18 mmol) of α-phellandrene (Fluka, 50%) in 2 mL of absolute ethanol was boiled under reflux for 11 h. After removal of the black precipitate by filtration, the filtrate was concentrated. The solid residue was stirred with ether and the solid recovered by filtration. ^{1}H NMR analysis of the brown solid showed it to be a mixture of **10** and **17** in the approximate ratio of 1:7.

(η^6-4,5,7,8-Tetramethyl[2₂](1,4)cyclophane)(η^6-[2₂](1,4)cyclophane)ruthenium(II) Bis(tetrafluoroborate) (13). To a solution of 13.1 mg (0.06 mmol) of silver tetrafluoroborate in 1.5 mL of acetone was added with stirring 14.7 mg (0.034 mmol) of **10**. The precipitate of silver chloride, which formed, was removed by filtration and the filtrate was added to a mixture of 35 mg (0.17 mmol) of [2₂](1,4)cyclophane (**12**) and 2 mL of trifluoroacetic acid. After the mixture had been boiled under reflux in a nitrogen atmosphere for 30 min, it was diluted with ether and the solid precipitate was collected by filtration. Nitromethane was added to dissolve the desired product and the remaining insoluble [2₂](1,4)cyclophane was removed by filtration. Addition of ether to the filtrate caused the separation of 20.3 mg (80%) of **13** as a yellow powder. For analysis, a sample was purified by recrystallization from an ether–nitromethane mixture to give yellow needles; mp dec >180 °C; ^{1}H NMR (CD_3NO_2) δ 6.99 (4 H, s, Ar H), 6.91 (4 H, s, Ar H), 5.80 (4 H, s, Ar H), 3.30 (4 H, m, CH_2), 3.23 (4 H, m, CH_2), 3.08 (4 H, m, CH_2), 2.94 (4 H, m, CH_2), 2.21 (12 H, s, ArCH_3).

Anal. Calcd for $C_{36}H_{40}Ru_2B_2F_8 \cdot H_2O$: C, 56.49; H, 5.53. Found: C, 56.49; H, 5.03.

Bis(η^6-4,5,7,8-tetramethyl[2₂](1,4)cyclophane)ruthenium-(II) Bis(tetrafluoroborate) (14). To a solution of 7.1 mg (0.036 mmol) of silver tetrafluoroborate in 1 mL of acetone was added 7.8 mg (0.018 mmol) of **10**. The precipitate of silver chloride, which formed, was removed by filtration and the filtrate was added to a mixture of 23.6 mg (0.089 mmol) of **5** and 1 mL of trifluoroacetic acid. After the mixture had been boiled under reflux in a nitrogen atmosphere for 30 min, it was diluted with ether and the yellow precipitate was collected by filtration. This gave 11.3 mg (79%) of a yellow solid; mp >300 °C dec; ^{1}H NMR (CD_3NO_2) δ 6.99 (4 H, s, Ar H), 5.80 (4 H, s, Ar H), 3.60–2.80 (16 H, m, CH_2), 2.24 (12 H, s, Ar CH_3), 2.09 (12 H, s, Ar CH_3).

Anal. Calcd for $C_{40}H_{48}Ru_2B_2F_8$: C, 59.79; H, 6.02. Found: C, 59.54; H, 5.93.

Formation of 22 from 13. To a solution of 34 mg (0.174 mmol) of silver tetrafluoroborate in 1.0 mL of acetone was added 29 mg (0.087 mmol) of bis(η^6-hexamethylbenzene)dichloro(di-μ-chloro)diruthenium(II)[14] with stirring. After the solution had been stirred for 20 min, the precipitate of silver chloride was removed by filtration and the filtrate was added to a mixture of 13 mg (0.017 mmol) of **13** in 1.0 mL of trifluoroacetic acid. The resulting mixture was boiled under reflux for 30 min and then diluted with ether. The resulting yellow solid was collected and characterized. Its ^{1}H NMR spectrum showed it to be very largely the known (η^6,η^6[2₂](1,4)cyclophane)bis(η^6-hexamethylbenzeneruthenium(II)) tetrakis(tetrafluoroborate) (**22**),[2] with an indication of the presence of a small amount of **21**.

(η^6-Hexamethylbenzene)(η^6-4,5,7,8-tetramethyl[2₂](1,4)-cyclophane)ruthenium(II) Bis(tetrafluoroborate) (24). To a solution of 74 mg (0.38 mmol) of silver tetrafluoroborate in 2 mL of acetone was added 63.2 mg (0.19 mmol) of bis(η^6-hexamethylbenzene)dichloro(di-μ-chloro)diruthenium(II)[14] with stirring. After 20 min, the precipitate of silver chloride was removed by filtration and the filtrate was added to a mixture of 50 mg (0.19 mmol) of **5** and 2 mL of trifluoroacetic acid. After the resulting mixture was boiled under reflux for 30 min, it was diluted with ether and the yellow precipitate was collected by filtration. Recrystallization of the yellow solid from a nitromethane–ether mixture gave 96 mg (94%) of yellow prisms: mp >200 °C dec; ^{1}H NMR (CD_3NO_2) δ 5.92 (4 H, s, Ar H), 3.52 and 3.10 (8 H, AA′BB′, CH_2), 2.51 (18 H, s, Ar CH_3), 2.16 (12 H, s, Ar CH_3).

Anal. Calcd for $C_{32}H_{42}B_2F_8$: C, 54.80; H, 6.04. Found: C, 54.64; H, 5.73.

(η^{12}-[2₂](1,4)Cyclophane)bis(cyclopentadienyl)diruthenium(II) Bis(tetrafluoroborate) (27). A solution of 61 mg (0.12 mmol) of (η^5-cyclopentadienyl)(η^6-[2₂](1,4)cyclophane)ruthenium(II) hexafluorophosphate (**26**)[31] and 222 mg (0.51 mmol) of (η^5-cyclopentadienyl)ruthenium(II) solvate (**25**) in 5 mL of acetonitrile was boiled under reflux for 12 h. After removal of the acetonitrile under reduced pressure, the residual solid was washed with dichloromethane and collected by filtration. Recrystallization of the solid from a nitromethane–ether mixture then gave 97 mg (99%) of tan needles; ^{1}H NMR (CD_3NO_2) δ 5.86 (8 H, s, Ar H),

5.29 (10 H, s, Cp H), 3.29 (8 H, s, CH_2).

Anal. Calcd for $C_{26}H_{26}Ru_2P_2F_{12}$: C, 37.60; H, 3.16. Found: C, 37.33; H, 3.19.

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Registry No. **2**, 623-24-5; **3**, 10519-84-3; **4**, 85883-16-5; **5**, 65304-59-8; **6**, 87012-45-1; **7**, 87012-46-2; **10**, 87050-02-0; **11**, 87012-48-4; **12**, 1633-22-3; **13**, 87012-50-8; **14**, 87012-52-0; **16**, 4221-98-1; **17**, 52462-29-0; **18**, 71303-83-8; **21**, 77089-81-7; **22**, 77089-86-2; **23**, 71861-30-8; **24**, 87012-54-2; **25**, 80049-61-2; **26**, 80049-69-0; **27**, 87039-17-6; $RuCl_3$, 10049-08-8; bis(η^6-hexamethylbenzene)dichloro(di-μ-chloro)diruthenium(II), 67421-02-7; thiourea, 62-56-6; 1,4-bis(chloromethyl)durene, 3022-16-0.

A New Olefin Synthesis. Synchronous Elimination of Nitro and Ester Groups or Nitro and Keto Groups from β-Nitro Esters or β-Nitro Ketones[1]

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A new synthesis of α,β-unsaturated nitriles (**13**), esters (**14**), ketones (**15**), or sulfones (**16**) [$R^1R^2C{=}CR^3Y$, Y = CN (**13**), Y = COOEt (**14**), Y = C(=O)R (**15**), Y = SO_2R (**16**)] starting from α-bromonitroalkanes (**1**) or α-chloronitroalkanes (**2**) is presented. The reaction of **1** or **2** with ethyl α-alkylcyanoacetate (**3**), diethyl α-alkylmalonate (**4**), ethyl α-alkylacetoacetate (**5**), α-alkyl β-diketones (**6**), or ethyl α-alkyl-α-sulfonylacetate (**7**) followed by elimination of ethoxycarbonyl and nitro groups or acetyl and nitro groups gives **13**, **14**, **15**, and **16**. As the carbon–carbon bond-forming step proceeds via a free radical chain process, the reaction is less sensitive to steric hindrance than usual ionic reactions like aldol condensations, and highly substituted olefins are readily prepared.

In recent years we have studied the synthetic applications of the aliphatic nitro group as a leaving group for olefin synthesis.[3] We have found that the coupling products (**8**, **9**, **10**, **11**, and **12**) between α-halonitroalkanes (**1**, **2**) and α-cyano esters (**3**), geminal diesters (**4**), β-keto esters (**5**), β-diketones (**6**), or α-sulfonyl esters (**7**) can be converted into α,β-unsaturated nitriles (**13**), esters (**14**), ketones (**15**), or sulfones (**16**), respectively, by elimination of nitro and ester groups, or nitro and keto groups.[1] We now wish to report additional experimental data for this useful olefin synthesis which further extend its synthetic utility. The first coupling step proceeds via a one-electron-transfer chain process,[4-6] which has been studied extensively by Russell and co-workers.[4] The reaction of α-halonitroalkanes with stable carbanions was originally reported by van Tamelen and Van Zyl in 1949,[7] and since then various nucleophiles have been reported to react with **1** or **2**.[4,5]

The second elimination step can be performed by heating **8**, **9**, **10**, or **12** with sodium bromide or lithium chloride to cause deethoxycarbonylative elimination or by treating **11** or **12** with reducing agents to cause deacetylative elimination. In general, the nitro group fails to serve as a leaving group in substitution or elimination reactions by ionic processes, but the elimination of the nitro group takes place readily to give olefins if electron-withdrawing groups exist at a position β to the nitro function.[8] Although a number of methods already exist for olefin synthesis,[9] the present method gives a useful addition to them. It is especially useful for the preparation of highly substituted olefins, because the carbon–carbon bond-forming step proceeds very rapidly and is less sensitive to steric hindrance than the usual ionic processes such as aldol condensations or S_N2 reactions. In the present transfor-

Table I. Conversion of 8a into 13a by Heating with MX

solvent	MX	temp, °C	time, h	yield of 13a, %[a]
HMPA	NaBr	120	1.5	75
Me_2SO	NaBr	140	3	54
DMF	NaBr	140	3	40
HMPA	NaCl	120	3	10
HMPA	LiCl	120	3	74
Me_2SO	LiCl	140	3	70

[a] Isolated yields.

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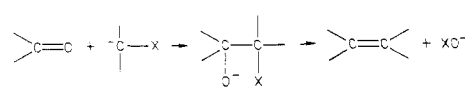
(9) A widely used method for olefin synthesis is carbonyl olefination represented by the following equation,



where X is PR_3, SiR_3, SR, SeR, etc.

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