trum which is substantially decreased in intensity on deuteration of the alcohol hydroxyl group.

The radical species was prepared by air oxidation of the parent quinol (Aldrich reagent grade) in a slightly basic ethanol solution (10^{-2} M). The X-band EPR and ENDOR spectra were recorded at 123 K with a Bruker ER200D spectrometer equipped with a Bruker ENDOR accessory by using procedures similar to those already described.[8] In recording the spectrum of the benzosemiquinone anion radical shown in Figure 1, we used a microwave power of 6.3 mW and 12.5-kHz frequency modulation of the incident microwave frequency radiation.

Hyde[14] has shown that, when the *p*-benzosemiquinone anion radical is rapidly rotating in liquid solution, an ENDOR band is observed at the isotropic coupling value of 2.37 G. On immobilization, however, three distinct bands are observed as illustrated in Figure 1, having absolute coupling values of 0.9 ± 0.1, 2.2 ± 0.1, and 3.4 ± 0.1 G. The EPR spectrum is also illustrated (inset a, Figure 1) and is identical with that already described by Hales.[15,16] The conclusion that the coupling values obtained represent the principal values of the hyperfine tensor is supported by the following observations: (i) The values are in the ratio 0.4:1.0:1.5, i.e., the expected ratio for the principal values of an α-proton hyperfine tensor.[9] (ii) The average value of 2.2 ± 0.1 G obtained from the sum of the three values is in good agreement with the isotropic value given above determined from the solution spectrum. (iii) Table I compares the experimental ENDOR hyperfine tensor values with theoretical values calculated by Atkins,[17] assuming that one principal axis of the local hyperfine tensor lies along the C–H bond direction (T_{CH}) with another axis parallel to the carbon p orbital (T_π). The excellent agreement between the experimental and theoretical values indicates that the principal axis system of the local hyperfine tensors do indeed lie along these directions.[18]

Figure 1 also illustrates an important difference in the shape of the bands observed for the principal components. a_2 and a_3 are relatively weak and broad bands when compared with a_1, which is present as a sharp and clearly defined band. Deuteration of the ethanol hydroxyl group leads to a considerable decrease in intensity of the a_1 band (unpublished data). We therefore attribute the intensity of the band in the protonated solvent to indicate hyperfine interaction from the solvent hydroxyl group. This confirms the original proposal of Hales, who attributed the increased EPR line width in protonated solvent to the formation of rigid hydrogen bonds between the alcohol hydroxyl and quinone carbonyl groups.[15,16]

The results presented here demonstrate the feasibility of obtaining the principal hyperfine tensor values from an organic radical's powder spectrum. The formation of rigid hydrogen bonds between the alcohol hydroxyl and the quinone carbonyl groups is also confirmed. Similar studies of in vivo radicals in powder type samples should prove valuable in elucidating the structure, environment, and orientation of these molecules in their biological habitat.

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Registry No. *p*-Benzosemiquinone anion radical, 3225-29-4.

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(17) Atkins, P. W. Ph.D. Thesis, University of Leicester, 1966.

(18) Böhme, U. R.; Wolf, H. C. *Chem. Phys. Lett.* **1972**, *17*, 582.

(19) Möbius, K.; van Willigen, H.; Maki, A. H. *Mol. Phys.* **1971**, *20*, 289.

(20) The strong absorption in the region 14–15.5 MHz can be attributed to the matrix peak usually observed in powder ENDOR spectra.[2] In contrast to previously reported matrix bands, it is composed of four resolved peaks. The sharp bands seen at the center in Figure 1 are slightly overmodulated. Observation at lower FM modulation (±30 KHz) shows the presence of four distinct bands (O'Malley, P. J.; Babcock, G. T., unpublished data). Observations of a structural matrix peak has previously been reported by Möbius et al.[19] and may be associated with the increased spectral resolution attainable by FM modulation and phase-sensitive detection.

(21) Sullivan, P. D.; Bolton, J. R.; Geiger, W. E. *J. Am. Chem. Soc.* **1970**, *92*, 4176.

Conversion of η^4,η^6-Bis(arene)ruthenium(0) Complexes to Cyclohexadienyl Analogues of Ruthenocene

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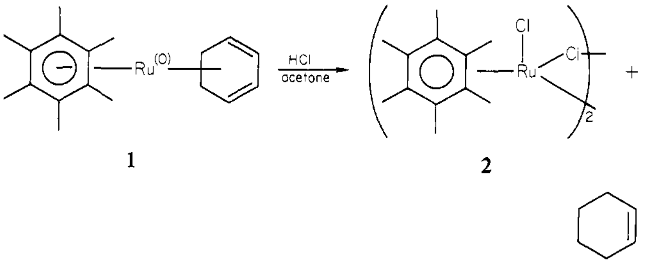
The reaction of (η^4-cyclohexadiene)(η^6-hexamethylbenzene)ruthenium(0) (**1**) with concentrated hydrochloric acid in acetone gives cyclohexene and the dimeric chloride **2**.[2] Previously, we have described using this basic reaction as a key step in a new, general method for synthesizing (η^6-[2_n]cyclophane)ruthenium(II) solvates and bis(η^6-[2_n]cyclophane)ruthenium(II) compounds.[3] Since, η^4,η^6-bis(arene)ruthenium(0) complexes are also well-known,[4-7] we have since investigated how such ruthenium(0) compounds behave toward acid. We now report that η^4,η^6-bis(arene)ruthenium(0) complexes react to yield cyclohexadienyl derivatives. These, in turn, readily undergo hydride reduction, so that the two-step sequence provides a convenient route for preparing cyclohexadienyl analogues of ruthenocene.



As shown in Scheme I, our first experiments were with (η^4-[2_2](1,4)cyclophane)(η^6-hexamethylbenzene)ruthenium(0) (**4**), which was prepared from **3** by reduction with aluminum in an aqueous sodium hydroxide–hexane mixture.[8,9] Treatment of **4** with concentrated hydrochloric acid in acetone then gave **5**. The skeletal structure assigned **5** was clearly suggested from its NMR spectra. However, elemental analysis of **5** showed the unexpected presence of the additional elements of hydrogen chloride. A single-crystal X-ray analysis confirmed the correctness of the skeletal assignment for **5** and showed the counterion to be the unusual hydrogen dichloride anion. This anion can readily be exchanged for other counterions such as PF_6^- and so is not an integral part of the organic moiety. In Figure 1 the molecular structure of **5** ($X^- = HCl_2^-$), as deduced from X-ray analysis, is presented.[9]

Reduction of **5** with Red-Al (sodium bis(2-methoxyethoxy)aluminum hydride) resulted in hydride attack on the hexa-

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(1) (a) University of Oregon. (b) Atlantic Research Laboratory.

(2) Grundy, S. L.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1982**, 379–380.

(3) Swann, R. T.; Boekelheide, V. *Abstr. Pap.–Am. Chem. Soc.* **1983**, *185th*, ORGN 33.

(4) Fischer, E. O.; Elschenbroich, Ch. *Chem. Ber.* **1970**, *103*, 162–172.

(5) Darensbourg, Y.; Muetterties, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 7425–7428.

(6) Muetterties, E. L.; Bleeke, J. R. *Acc. Chem. Res.* **1979**, *12*, 324–331.

(7) Huttner, G.; Lange, S. *Acta Crystallogr., Sect. B* **1972**, *B28*, 2049–2060.

(8) We thank Professor Muetterties for suggesting this method of reduction. Richard Voegeli (unpublished work) has also shown that **4** can be prepared from **3** in good yield by bulk electrolysis.

(9) All new compounds being reported have been fully characterized and thier composition and spectral properties are in agreement with their assigned structures. Compound **5** crystallized in the monoclinic system, $P2_1/n$ with a = 18.362 (2) Å, b = 14.946 (2) Å, c = 9.219(1) Å, β = 94.79 (1)° (T = 24 °C, Mo Kα, λ_{a1} = 0.7093 Å) U = 2521.2 Å^3, Z = 4, D_m = 1.43 (1), D_x = 1.434 g cm^{-3}. The structure was solved by the heavy-atom method and refined to R = 0.044 for 6242 reflections with $T > 3\sigma(I)$. Key information regarding the properties of these new compounds and the details of the X-ray crystallographic analysis of **5** are given in the supplementary material.

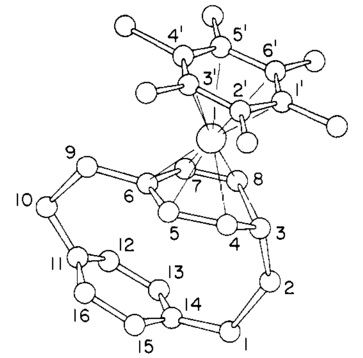
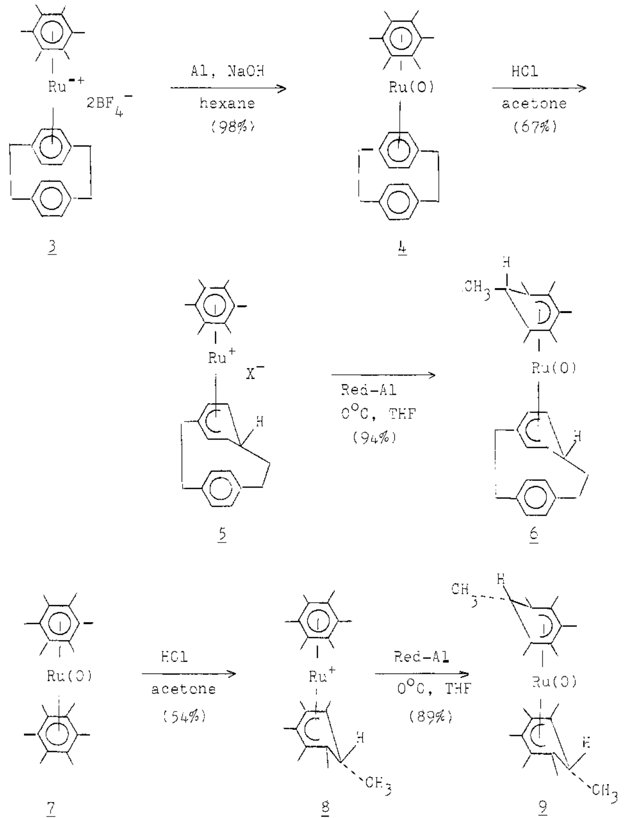


Figure 1. (η-Hexamethylbenzene)(η^5-3H-[2$_2$](1,4)cyclophane)ruthenium(II) hydrogen dichloride (**5**). A view of the metal-organic ion (H atoms omitted). Ru-C bonds range from 2.17 (1) to 2.24 (1) Å. Some C-C distances: 3-2, 1.56 (2); 3-4, 1.53 (2); 3-8, 1.51 (2); 4-5, 1.42 (2); 7-8, 1.40 (2); 5-6, 1.41 (2); 6-7, 1.42 (2) Å. Other C-C distances and angles are generally consistent with the proposed formulation.

Scheme I



methylbenzene ring to give the cyclohexadienyl analogue of ruthenocene, compound **6**, as relatively air-stable, yellow crystals.

To test the generality of this reaction sequence bis(hexamethylbenzene)ruthenium(0)[4] was then carried through in the same fashion to give **8** and **9**, both being formed in good yield.

Although we have no firm evidence regarding the mechanism of the reaction of these η^4,η^6-bis(arene)ruthenium(0) compounds with acid, there occurred in each reaction an immediate formation of a deep red color that rapidly faded. One can speculate that the red color is associated with the formation of a hydridoruthenium intermediate. Transfer of hydrogen then from ruthenium to an arene ring is an obvious possible explanation for the formation of **5** and **8**. For **5** the choice of transfer of hydrogen to the cyclophane moiety rather than to the hexamethylbenzene is probably determined by the relief of strain of the cyclophane ring. Also, the X-ray analysis of **5** shows the hydrogen has been added in an endo fashion as would be predicted for transfer from the ruthenium atom. Since Red-Al reduction places hydrogen exo,[3] the overall consequence is that both **6** and **9** must have one "extra" hydrogen exo and the other endo. The assignment of infrared stretching frequencies to the endo and exo C-H bonds in metal complexes of cyclohexadienyl anions has been a subject of controversy.[10-13] However, it is now generally agreed that *endo*-C-H bonds absorb in the 2950-cm^{-1} region whereas *exo*-C-H bonds absorb around 2750 cm^{-1}, and this is in accord with our infrared measurements of **5**, **6**, **8**, and **9** and the X-ray analysis of **5**.

The NMR spectral data for **6** and **9** require a high degree of symmetry, but whether this is due to free rotation about the π-metal bonds or due rather to frozen conformations, such as those drawn for **6** and **9**, has not yet been determined.

The formation of **5** and **6** represent the first [2$_n$]cyclophane having a cyclohexadienyl anion deck. Of interest is the possible extension of these methods to form [2$_n$]cyclophanes, where both decks are cyclohexadienyl moieties, as well as the polymers of such cyclophanes with transition metals. These results also are of interest in relation to the recent studies of the bis(pentadienyl)iron analogues of ferrocene.[14,15]

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Registry No. 3, 77089-82-8; 4, 88453-36-5; 5 ($X^- = PF_6^-$), 88453-38-7; 5 ($X^- = HCl_2^-$), 88453-43-4; 6, 88453-39-8; 7, 32732-05-1; 8, 88453-41-2; 9, 88453-42-3; HCl, 7647-01-0.

Supplementary Material Available: Properties of the new compounds and the X-ray crystal structure analysis of (η^6-hexamethylbenzene)(η^5-3H-[2$_2$](1,4)cyclophane)ruthenium(II) hydrogen dichloride (**5**), $C_{28}H_{36}Cl_2Ru$ (83 pages). Ordering information is given on any current masthead page.

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(10) Jones, D.; Wilkinson, G. *J. Chem. Soc.* **1964**, 2479-2481. Jones, D.; Pratt, L.; Wilkinson, G. *Ibid.* **1962**, 4458-4463.

(11) Khand, I. U.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc. C* **1969**, 2024-2030.

(12) Bird, P. H.; Churchill, M. R. *Chem. Commun.* **1967**, 777-778.

(13) Treichel, P. M.; Shubkin, R. L. *Inorg. Chem.* **1967**, *6*, 1328-1333.

(14) Wilson, D. R.; DiLullo, A. A.; Ernst, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 5928-5930.

(15) Böhn, M. C.; Eckert-Makić, M.; Ernst, R. D.; Wilson, D. R.; Gleiter, R. *J. Am. Chem. Soc.* **1982**, *104*, 2699-2707.

X-ray Crystal Structures of the Diphenylphosphide and -arsenide Anions: Use of a Crown Ether To Effect Complete Metal Cation and Organometalloid Anion Separation

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The synthesis and characterization of two-coordinate derivatives of heavier main-group elements have been the subject of intense studies during the past decade.[2] For phosphorus such compounds include the stable dialkyl and diamide radicals,[3] the phosphabenzenes,[4] two-coordinate cationic species,[5] compounds containing double bonds to carbon or nitrogen,[6] and more recently, compounds having stable phosphorus-phosphorus double bonds.[7] The al-

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(1) On leave from the Department of Chemistry, Peking University, Beijing, China.

(2) Fluck, E. *Top. Phosphorus Chem.* **1980**, *10*, 193-284.

(3) Gynane, M. J. S.; Hudson, A.; Lappert, M. F.; Power, P. P.; Goldwhite, H. *J. Chem. Soc., Dalton Trans.* **1980**, 2428-2433; *J. Chem. Soc., Chem. Commun.* **1976**, 623. Cetinkaya, B.; Hudson, A. H.; Lappert, M. F.; Goldwhite, H. *Ibid.* **1982**, 609-610.

(4) Markl, G. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 846-847. Markl, G. *Phosphorus Sulfur* **1977**, *3*, 77-108.