

[CONTRIBUTION FROM THE INSTITUTE FOR INORGANIC CHEMISTRY, UNIVERSITY OF MUNICH, MUNICH, GERMANY]

New Cyclopentadienyl Complexes of Rhodium

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RECEIVED JULY 29, 1963

The di- π -cyclopentadienylrhodium(III) cation reacts with lithium phenyl to give π -cyclopentadienyl-(1-*exo*-phenylcyclopentadiene)-rhodium, I, which can be oxidized by oxygen or H₂O₂ to the π -cyclopentadienyl-(π -phenylcyclopentadienyl)-rhodium(III) cation. Compound I also reacts with bromine to give polymeric [(C₅H₅)RhBr₂]_x, which readily reacts with pyridine to yield (C₅H₅)RhBr₂(py). π -Cyclopentadienyl-(1-*exo*-cyclopentadienylcyclopentadiene)-rhodium and a compound of unknown structure, Rh₂(C₅H₅)₆, have been obtained from the reaction of the dicyclopentadienylrhodium cation with sodium cyclopentadienide.

The di- π -cyclopentadienylcobalt(III) cation is known to react with such nucleophilic agents as lithium aluminum hydride² and lithium alkyls and aryls³ to form π -cyclopentadienyl-(cyclopentadiene)-cobalt and π -cyclopentadienyl-(1-aryl (or alkyl) cyclopentadiene)-cobalt. It was also found to react with sodium cyclopentadienide to give, instead of the simple addition product, the binuclear Co₂C₂₅H₂₄.⁴

Except for the reaction of the di- π -cyclopentadienylrhodium(III) cation with lithium aluminum hydride to yield π -cyclopentadienyl-(cyclopentadiene)-rhodium,² no other reactions of the rhodium compound with nucleophilic agents have been investigated. It was therefore of interest to study its reactions with lithium aryls and sodium cyclopentadienide in order to compare the reactivities of the cations and the properties of the products of these reactions with the analogous cobalt derivatives.

Experimental

Di- π -cyclopentadienylrhodium(III) Tribromide.—The synthesis was carried out in a 500-ml., three-necked, round-bottom flask fitted with a nitrogen inlet, a dropping funnel, a reflux condenser, and a magnetic stirrer. A solution of 22 ml. of ethyl bromide in 60 ml. of ether was added slowly to 6.0 g. of magnesium turnings in a nitrogen atmosphere. After the magnesium had been consumed, 22 ml. of freshly distilled cyclopentadiene in 60 ml. of benzene was added to the solution, and the mixture was stirred at room temperature for 1 hr. and then refluxed for 4 hr. The solution was cooled to room temperature, and 8.0 g. of anhydrous RhCl₃ was added. The heterogeneous mixture was stirred at room temperature for 18 hr. and then refluxed for 1 hr. The excess Grignard reagent was hydrolyzed in air with 150 ml. of water, and the mixture was filtered. After separation of the aqueous layer from benzene, a solution of KBr and Br₂ (1:1) was added to precipitate the product, which was washed several times with small amounts of water. The yellow compound was dried under vacuum and identified by analysis and from its previously reported properties⁵; yield, 16.7 g. (93%).

π -Cyclopentadienyl-(1-*exo*-phenylcyclopentadiene)-rhodium.—[Rh(C₅H₅)₂Br₃ (1.0 g.)] was stirred at room temperature in 10 ml. of tetrahydrofuran (THF) with several zinc pellets for 24 hr. This treatment reduced the tribromide anion to a mixture of ZnBr₃⁻ and ZnBr₂²⁻ as determined from analyses. The gray precipitate was filtered and then washed with small amounts of THF. This compound was placed in 50 ml. of ether in a three-necked, round-bottom flask in a nitrogen atmosphere. To this vigorously stirred suspension was added 4 mmoles of LiC₅H₅ in 4 ml. of ether. After stirring for 2 min., several small pieces of Dry Ice and then 50 ml. of water were added. The yellow ether layer was separated and the ether removed with a water aspirator. From the residue, biphenyl was sublimed at 65° and then the product (0.45 g., 69%) at 95–100° under high vacuum. The yellow compound was chromatographed on an alumina column in cyclohexane and again sublimed; m.p. 118.5–119.5°. The crystals are stable in air, and in solution it decomposes only very slowly. It is soluble in most common organic solvents, but is only moderately soluble in *n*-pentane at room temperature; at –78°, it crystallizes from solution; infrared spectrum in KBr: 3040 (w), 3012 (w), 2924 (w), 1592 (m), 1497 (w), 1484 (s), 1447 (s), 1418 (w), 1404 (m), 1377 (w), 1368 (w), 1342 (m), 1324 (m),

1299 (m), 1252 (m), 1239 (m), 1199 (m), 1175 (m), 1153 (w), 1101 (s), 1076 (s), 1064 (s), 1027 (m), 1003 (s), 990 (s), 951 (w), 943 (w), 912 (w), 870 (m), 859 (w), 842 (s), 818 (s), 791 (vs), 782 (vs), 747 (vs), 700 (vs) cm.⁻¹.

Anal. Calcd. for [(C₅H₅)(1-*exo*-C₆H₅C₅H₅)Rh]: C, 61.94; H, 4.88; Rh, 33.18; mol. wt., 310. Found: C, 61.75; H, 4.76; Rh, 33.2; mol. wt., 308 (osmometric in benzene).

π -Cyclopentadienyl-(π -phenylcyclopentadienyl)-rhodium(III) Hexafluorophosphate.—(C₅H₅)(1-*exo*-C₆H₅C₅H₅)Rh (200 mg.) in 8 ml. of 2 *N* HCl was heated to boiling in a test tube until no further change took place. Black particles were removed from the orange solution by filtration. After removing the water under high vacuum, the brown oily residue was dissolved in about 10 drops of water. Upon adding solid NH₄PF₆, a brown oil formed which crystallized when the glass was scratched with a rod. The mixture was then filtered leaving brown crystals. These were dissolved in acetone (~2 ml.), and the solution was treated with activated charcoal three times. Crystals were precipitated by the addition of ether (~12 ml.) and seeding with a crystal of the compound. The precipitation was repeated several times until white crystals of the product were obtained. These (90 mg., 31%) were dried under vacuum; infrared spectrum in KBr: 3135 (s), 2933 (w), 1887 (w), 1582 (w), 1458 (s), 1420 (s), 1393 (m), 1309 (w), 1211 (w), 1179 (w), 1109 (w), 1076 (m), 1056 (w), 1030 (m), 1012 (m), 970 (w), 945 (w), 905 (s), 831 (vs), 767 (vs), 698 (s), 693 (s) cm.⁻¹. The cation has properties very similar to those of the unsubstituted dicyclopentadienylrhodium(III) cation.

Anal. Calcd. for [(C₅H₅)(C₆H₅C₅H₅)Rh]PF₆: C, 42.29; H, 3.11; Rh, 22.67; P, 6.83; F, 25.11. Found: C, 42.50; H, 3.20; Rh, 23.0; P, 6.85; F, 24.90.

π -Cyclopentadienyl-dibromorhodium(III).—To a solution of 200 mg. of (C₅H₅)(1-*exo*-C₆H₅C₅H₅)Rh in 15 ml. of *n*-hexane was added a hexane solution of bromine. A dark red compound precipitated, was separated by filtration, and washed several times with hexane. After drying, 0.21 g. (98%) of the product was obtained. The compound is insoluble in pentane, benzene, methylene chloride, acetone, methanol, and water. Its solubility properties strongly suggest that the compound is a polymer. It is very stable in air.

Anal. Calcd. for [(C₅H₅)RhBr₂]: C, 18.31; H, 1.54; Rh, 31.40; Br, 48.76. Found: C, 18.38; H, 1.68; Rh, 31.3; Br, 48.6.

Infrared spectrum in KBr: 3106 (s), 2941 (w), 1414 (s), 1348 (w), 1057 (w), 1000 (w), 847 (s), 820 (m), 696 (w) cm.⁻¹.

[(C₅H₅)RhI₂]_x, prepared by the same method, has the following spectrum: 3086 (m), 2924 (w), 1406 (s), 1346 (w), 1050 (w), 990 (w), 840 (s), 818 (s) cm.⁻¹.

π -Cyclopentadienyl-(pyridine)-dibromorhodium(III).—[(C₅H₅)RhBr₂]_x was dissolved in pyridine. After filtering, the solution was evaporated to dryness at room temperature under vacuum. The orange residue was dissolved in methylene chloride, and the solution was filtered through cellulose. The addition of *n*-pentane to the solution precipitated the product which was rinsed with pentane and dried under high vacuum. The orange product, which was obtained in quantitative yield and decomposes over 220°, is moderately soluble in pyridine, methylene chloride, acetone, and methanol, and insoluble in water and pentane. The compound is very stable in the solid state and decomposes only very slowly in solution; infrared spectrum in KBr: 3086 (s), 2933 (w), 1603 (s), 1482 (m), 1445 (s), 1412 (s), 1353 (w), 1232 (w), 1216 (m), 1152 (w), 1104 (w), 1070 (s), 1043 (w), 1014 (m), 950 (m), 939 (w), 850 (s), 822 (m), 758 (s), 690 (s) cm.⁻¹.

Anal. Calcd. for [(C₅H₅)RhBr₂(NC₅H₅)]: C, 29.50; H, 2.48; N, 3.44; Rh, 25.30. Found: C, 30.12; H, 2.73; N, 3.70; Rh, 25.50.

π -Cyclopentadienyl-(1-*exo*-cyclopentadienylcyclopentadiene)-rhodium.—[Rh(C₅H₅)₂Br₃ (1.0 g.)] was stirred with several zinc pellets in THF at room temperature for 24 hr. After washing with THF, the gray powder was added to a suspension of sodium cyclopentadienide prepared from 0.20 g. of sodium pulver and

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(2) M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3753 (1959).(3) E. O. Fischer and G. E. Herberich, *Chem. Ber.*, **94**, 1517 (1961).(4) E. O. Fischer, W. Fellman, and G. E. Herberich, *ibid.*, **95**, 2254 (1962).(5) F. A. Cotton, R. O. Whipple, and G. Wilkinson, *J. Am. Chem. Soc.*, **75**, 3586 (1953).

1.5 ml. of freshly distilled cyclopentadiene in 40 ml. of ether. The mixture was stirred under nitrogen for 30 min. at room temperature and then filtered. The ether was evaporated from the yellow solution under vacuum, and the product was sublimed at 60° under high vacuum from the oily residue. Resublimation of the yellow compound yielded about 10 mg. of the pure substance, m.p. 79–80°; infrared spectrum in KBr: 3040 (w), 2882 (w), 1779 (w), 1689 (w), 1587 (w), 1423 (w), 1407 (m), 1366 (s), 1357 (s), 1324 (m), 1253 (w), 1245 (w), 1235 (m), 1188 (s), 1153 (w), 1129 (w), 1102 (s), 1060 (s), 1033 (m), 1003 (s), 992 (s), 983 (s), 946 (s), 926 (m), 902 (m), 895 (s), 835 (w), 875 (m), 787 (vs), 733 (s), 709 (w), 689 (m), 678 (s) cm⁻¹. Its solubility in organic solvents is very similar to that of (C₅H₅)(1-*exo*-C₆H₅C₅H₅)Rh.

Anal. Calcd. for [(C₅H₅)(1-*exo*-C₆H₅C₅H₅)Rh]: C, 60.40; H, 5.07; Rh, 34.53; mol. wt., 298. Found: C, 61.06; H, 5.05; Rh, 34.3; mol. wt., 305 (osmometric in benzene)

The brown oil remaining after the sublimation was dissolved in *n*-pentane at room temperature and under nitrogen. The solution was filtered and cooled to -78°, whereupon pale yellow crystals of Rh₂(C₅H₅)₆ precipitated. After drying in high vacuum for 2 hr., an approximately 70% yield of the dimer was obtained. In air the compound decomposes slowly in the solid state but quite rapidly in solution. The solid begins to decompose above 70° and could not be sublimed. It has solubility properties essentially the same as the monomer; infrared spectrum in KBr: 3185 (w), 3040 (m), 2916 (s), 2849 (m), 1767 (w), 1425 (w), 1406 (m), 1370 (m), 1342 (m), 1326 (w), 1256 (w), 1238 (w), 1216 (w), 1191 (m), 1103 (s), 1059 (s), 1035 (m), 1005 (s), 992 (s), 948 (m), 892 (w), 871 (w), 852 (w), 824 (m), 789 (vs), 723 (m) cm⁻¹.

Anal. Calcd. for Rh₂(C₅H₅)₆: C, 60.40; H, 5.07; Rh, 34.53; mol. wt., 596. Found: C, 60.14; H, 5.19; Rh, 34.4; mol. wt., 605 (osmometric in benzene).

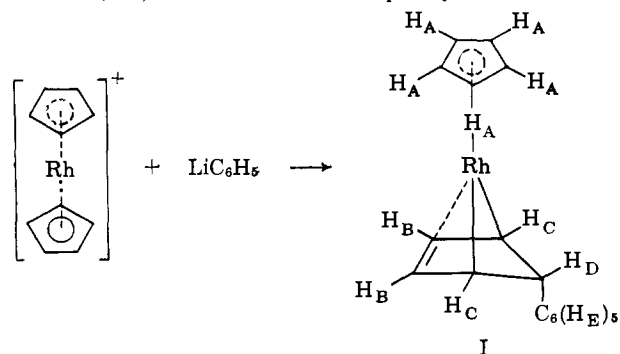
The infrared spectra were obtained with a Perkin-Elmer, Model 21, spectrophotometer with NaCl optics and the proton nuclear magnetic resonance spectra with a Varian-A-60 spectrophotometer using tetramethylsilane as the external standard.⁶

Discussion

Di- π -cyclopentadienylrhodium(III) tribromide had originally been prepared by the reaction of rhodium(III) acetylacetonate with cyclopentadienylmagnesium bromide in benzene, but no yield was reported.⁵ In the present study, the yields obtained using this method were always small. The preparation of rhodium(III) acetylacetonate also gave unsatisfactory yields.⁷ For these reasons, another method of synthesis was sought.

It was found that insoluble anhydrous rhodium trichloride suspended in a mixture of ether and benzene reacts with cyclopentadienylmagnesium bromide within 24 hr. to give the dicyclopentadienylrhodium(III) cation in 93% yield. Unlike the dicyclopentadienylcobalt(III) cation, the rhodium compound could not be precipitated with perchlorate ion. This salt of the cobalt cation was fairly soluble in organic solvents and thus allowed a homogeneous reaction with the nucleophilic agents. In the case of rhodium, the insoluble ZnBr₃⁻ and ZnBr₄²⁻ salts were used, and the heterogeneity of the reaction mixtures may account for the difference in yields and even in products between the cobalt and rhodium reactions.

π -Cyclopentadienyl-(1-*exo*-phenylcyclopentadiene)-rhodium, as well as the analogous cobalt complex,³ was prepared by the reaction of the dicyclopentadienylrhodium(III) cation with lithium phenyl in ether.



(6) For the spectra, we thank Miss A. Bühler and Mrs. H. Dove.

(7) F. P. Dwyer and A. M. Sargeson, *J. Am. Chem. Soc.*, **75**, 984 (1953).

The yields for the rhodium reaction were lower, perhaps because of the insolubility of the dicyclopentadienylrhodium salt in ether.

The structure of the analogous cobalt compound, which was originally proposed on the basis of infrared and nuclear magnetic resonance spectroscopic studies,^{2,3} showed the phenyl group in the *endo* position, and the postulated mode of bonding of the lower ring to the cobalt was through the two double bonds of the diene system. A recent X-ray investigation⁸ of this compound has shown, however, that the phenyl group occupies the *exo* position relative to cobalt and that the "cyclopentadiene" ring to cobalt bonding is more accurately represented by one π - and two σ -bonds. The fact that the carbon of the cyclopentadiene ring that is not bound to the metal is bent away from the cobalt atom accounts for the absence of a high-field proton in the n.m.r. spectrum and the absence of an intense C-H_D stretching absorption at 2780 cm⁻¹. These data were originally interpreted to mean that H_D was in the *exo* position.

Although the X-ray study has demonstrated the stereochemistry of the cobalt complex, it is by no means certain that the rhodium analog has the same configuration. For this reason X-ray diffraction powder photographs of (C₅H₅)(1-*exo*-C₆H₅C₅H₅)Co and (C₅H₅)(1-*exo*-C₆H₅C₅H₅)Rh were compared. They show that the crystals are isomorphous and have orthorhombic symmetry.⁹ This evidence is a very good indication that the rhodium compound is isostructural with the cobalt complex (see structure I). That the infrared spectra of these two compounds are virtually identical also supports this structural assignment.

The n.m.r. spectrum of the diamagnetic rhodium complex I shows the presence of five different protons, whose assignments are given in Table I. These assignments were made on the basis of intensity, shielding, and spin-spin splitting arguments which have been already presented for π -cyclopentadienyl-(cyclopentadiene)-rhodium and related cobalt compounds.^{2,10} It should be noted that ¹⁰³Rh has a nuclear spin of 1/2, which produces the H_A doublet and some of the other multiplets.

π -Cyclopentadienyl-(π -phenylcyclopentadienyl)-rhodium(III) Cation.—Since it was known that π -cyclopentadienyl-(cyclopentadiene)-cobalt could be oxidized to Co(C₅H₅)₂⁺ in air,² several attempts to prepare substituted dicyclopentadienylcobalt cations by oxidizing (C₅H₅)(1-RC₅H₅)Co compounds were made. In every case, either total decomposition of the complex resulted or cleavage of R gave Co(C₅H₅)₂⁺.³

Like the analogous cobalt compound, π -cyclopentadienyl-(cyclopentadiene)-rhodium was readily oxidized to Rh(C₅H₅)₂⁺,^{2,11} but in contrast to (C₅H₅)(1-*exo*-C₆H₅C₅H₅)Co, (C₅H₅)(1-*exo*-C₆H₅C₅H₅)Rh can be oxidized by either oxygen or H₂O₂ in 2 *N* HCl to the substituted cation (C₅H₅)(C₆H₅C₅H₄)Rh(III). It can be readily precipitated as the triiodide or tribromide in an almost quantitative yield; however, owing to the presence of higher halides, the analyses of these compounds were always about 1% in error. Precipitation of the cation with hexafluorophosphate anion from a very small amount of water gave pure [(C₅H₅)(C₆H₅C₅H₄)Rh]PF₆. The relatively high solubility of this compound in water reduced the yields to 31%.

The infrared spectrum of the compound shows characteristic absorption bands for the cyclopentadienyl and phenyl groups and is very similar to that of the

(8) M. R. Churchill and R. Mason, *Proc. Chem. Soc.*, 112 (1963).

(9) The authors are grateful to E. Paulus for these X-ray investigations.

(10) H. P. Fritz and H. J. Keller, *Chem. Ber.*, **95**, 2259 (1962).

(11) E. O. Fischer and U. Zahn, *ibid.*, **92**, 1624 (1959).

analogous cobalt complex $[(C_5H_5)(C_6H_5C_5H_4)Co]PF_6$, which was prepared by a different method.¹²

The n.m.r. spectrum of the triiodide salt shows the presence of phenyl and cyclopentadienyl protons, both of which are shifted to lower fields as a result of the positive charge on the ion. The proton assignments and their τ -values are given in Table I.

TABLE I
PROTON NUCLEAR MAGNETIC RESONANCE SPECTRA

τ	Relative intensity	Structure	Assignment
$(C_5H_5)(1-exo-C_6H_5C_5H_5)Rh$ in CCl_4			
3.02	5	Multiplet	H_E
4.81	5	Doublet	H_A
4.86	2	Multiplet	H_B
6.02	1	Triplet	H_D
6.38	2	Multiplet	H_C
$[(C_5H_5)(C_6H_5C_5H_4)Rh]I_3$ in acetone			
2.61	5	Multiplet	Phenyl H's
3.34-3.85	4	Multiplet	C_6H_4 H's
4.04	5	Doublet	C_5H_5 H's
$(C_5H_5)(1-exo-C_6H_5C_5H_5)Rh$ in C_6D_6			
3.69-4.35	3	Multiplet	H_E
4.96	5	Doublet	H_A
5.10	2	Multiplet	H_B
6.13	1	Triplet	H_D
6.55	2	Multiplet	H_C
7.46	2	Multiplet	H_G

π -Cyclopentadienyldibromorhodium(III).—This dark red compound precipitates immediately when *n*-hexane solutions of $(C_5H_5)(1-exo-C_6H_5C_5H_5)Rh$ and bromine are mixed. Since it is insoluble in all common solvents, it appears that it has a polymeric structure, $[(C_5H_5)RhBr_2]_x$, in which the single units are linked together by bromide bridges. The infrared spectrum of the compound shows only a few weak bands in addition to those characteristic of the π -cyclopentadienyl group. Iodine also reacts with $(C_5H_5)(1-exo-C_6H_5C_5H_5)Rh$ to give the analogous iodide $[(C_5H_5)RhI_2]_x$, which was only identified by its infrared spectrum.

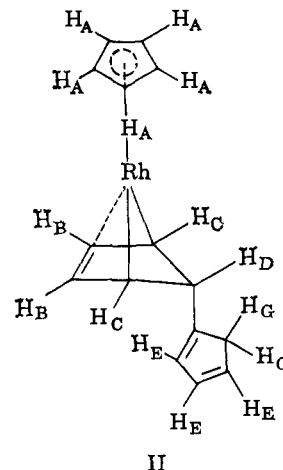
π -Cyclopentadienyl-(pyridine)-dibromorhodium(III).—As is common for compounds with halide bridges, $[(C_5H_5)RhBr_2]_x$ reacts with pyridine very rapidly at room temperature to give $(C_5H_5)RhBr_2(py)$. The monomeric nature of this compound has not been proved because of its low solubility in common solvents, but such a structure is reasonable since it allows rhodium to attain the next inert gas configuration. Its low solubility in organic solvents and its insolubility in water are consistent with the highly polar but nonionic nature of the compound.

π -Cyclopentadienyl-(1-*exo*-cyclopentadienylcyclopentadiene)-rhodium.—The dicyclopentadienylcobalt(III) cation reacts with sodium cyclopentadienide to give $Co_2C_{25}H_{24}$ in which [π -cyclopentadienyl-(cyclopentadiene)-yl] groups are bound to the 2- and 4-positions of cyclopentadiene.^{4,10} It was therefore of interest to determine whether the dicyclopentadienyl-

rhodium cation also formed this unusual bridged compound.

The dicyclopentadienylnrhodium(III) cation reacts with sodium cyclopentadienide in ether at room temperature to give a small yield of $(C_5H_5)(1-exo-C_6H_5C_5H_5)Rh$. It is stable in air in the solid state but decomposes slowly in solution.

The compound is believed to have structure II. This assignment has been made primarily on the basis of



II

n.m.r. results shown in Table I. The H_A , H_B , H_C , and H_D protons can be readily assigned from intensity data. Comparison of the τ -values of these protons with those of the corresponding protons in $(C_5H_5)(1-exo-C_6H_5C_5H_5)Rh$, I, supports this assignment. Moreover, the similarity of the position and splitting of the H_D proton in both structures I and II suggests that the cyclopentadienyl ring is likewise bonded in the *exo* position. The H_E protons appear in the usual olefinic proton region, and their relative intensity indicates the presence of only three such protons. This suggests that the cyclopentadienyl ring is bonded through an unsaturated carbon. Because of the complicated splitting of both the H_E and H_G protons, it is not clear whether the cyclopentadienyl ring is bonded through the 2- or 3-position. The two H_G protons have a τ -value of 7.46 which correlates well with 7.65 found for the analogous protons in π -cyclopentadienyl-(1-indenylcyclopentadiene)-cobalt.¹⁰

In addition to the monomer, a compound having the composition $Rh_2(C_5H_5)_6$ was also isolated from the reaction mixture. Because of the instability of its solutions, n.m.r. spectra of it were not reproducible and gave little indication of the structure of the compound. One structural possibility is the Diels-Alder adduct resulting from the condensation of the cyclopentadienyl rings of two $(C_5H_5)(1-exo-C_6H_5C_5H_5)Rh$ molecules. If this were indeed the case, one might expect the yields of the monomer to change with an increase or decrease in reaction time. This, however, was not observed and suggests that $(C_5H_5)(1-exo-C_6H_5C_5H_5)Rh$ and $Rh_2(C_5H_5)_6$ are formed by independent mechanisms.

Acknowledgment.—R. J. A. wishes to thank the National Science Foundation for a Postdoctoral Fellowship.