Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

ORGANOMETALLIC CHEMISTRY OF THE TRANSITION METALS
XXVII. SOME NEW RHODIUM COMPLEXES OF ALLENE PENTAMER (1,2,5,6,8-PENTAMETHYLENECYCLODECANE)*

R. B. KING AND PRAMESH N. KAPOOR**

Department of Chemistry, University of Georgia, Athens, Georgia 30601 (U.S.A.)

(Received June 9th, 1971)

SUMMARY

Several reactions of rhodium(I) complexes of 1,2,5,6,8-pentamethylenecyclodecane (allene pentamer, $C_{15}H_{20}$) are described. Reaction of the chloride $C_{15}H_{20}RhCl$ with (pentafluorophenyl)lithium in diethyl ether gives the yellow crystalline σ-pentafluorophenyl derivative $C_{15}H_{20}RhC_6F_5$, apparently the first known example of a derivative with a transition metal–carbon σ-bond where all of the other ligands are coordinated carbon–carbon double bonds. Reaction of $C_{15}H_{20}RhCl$ with sodium cyclopentadienide in tetrahydrofuran solution gives yellow waxy $C_{15}H_{20}RhC_5H_5$ shown by its NMR spectrum to have a *tetrahapto*-1,2,5,6,8-pentamethylenecyclodecane ligand and a *pentahapto*-cyclopentadienyl ligand. The predominant ion in the mass spectrum of $C_{15}H_{20}RhC_5H_5$ is $C_{15}H_{20}Rh^+$ which is formed by loss of C_5H_5 from the molecular ion. Reaction of $C_{15}H_{20}RhCl$ with stannous chloride in diethyl ether gives yellow $C_{15}H_{20}RhSnCl_3$. Reaction of $C_{15}H_{20}RhCl$ with silver hexafluorophosphate in acetone solution gives the yellow salt $[C_{15}H_{20}Rh][PF_6]$. This salt reacts with carbon monoxide at atmospheric pressure to give the yellow monocarbonyl $[C_{15}H_{20}RhCO][PF_6]$, which can also be obtained by reaction of $C_{15}H_{20}$-$RhCl$ with carbon monoxide in boiling ethanol followed by reaction with ammonium hexafluorophosphate in aqueous acetone.

INTRODUCTION

Rhodium(I) complexes of the type $(olefin)_4RhX$ (X = halide or other one-electron donor) have the favored 18-electron rare gas configuration[2]. However, the rhodium(I)–olefin bonds in most such complexes are relatively weak. Thus, complexes of the type $(diene)_2RhCl$ (diene = conjugated 1,3-diene such as butadiene) readily lose the coordinated diolefin slightly above room temperature[3]. Therefore an extensive chemistry of $(diene)_2RhX$ derivatives has not been developed.

These observations suggest that an extensive chemistry of complexes of the $(olefin)_4RhX$ type requires a special type of olefin for sufficient stability of the rho-

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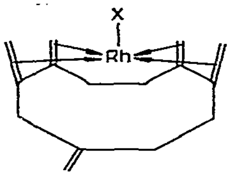
* For part XXVI see ref. 1.

** Post-doctoral research associate 1968–1969, 1970–1971.

dium–olefin bonds. One possibility for stabilization of compounds of the type (olefin)$_4$RhX is for all coordinated olefin ligands to be part of the same tetraolefin molecule. The chelate effect[4] would then confer special stability on species of the type (tetraene)RhX. In particular, transformations of the X group without complete rupture of the rhodium–olefin bonds would then become feasible.

Tetraolefins with all four carbon–carbon double bonds in positions suitable for simultaneous bonding to a single metal atom are rare. One conceivable candidate, cyclooctatetraene, instead forms rhodium(I) complexes such as $[C_8H_8RhCl]_2$ in which only two of the four double bonds of a cyclooctatetraene unit (those in the 1,5-positions) are bonded to a single rhodium atom[5]. The recent discovery by Otsuka, Tani and Nakamura[6] of the stable complex 1,2,5,6,8-pentamethylenecyclodecanerhodium(I) chloride, $C_{15}H_{20}RhCl$ [(I)X=Cl], thus appeared to provide an unusual opportunity to study some chemical transformations in systems of the type (tetraene)RhX. The complex $C_{15}H_{20}RhCl$ [(I) X=Cl] is readily preparable from certain rhodium(I) complexes (*e.g.* $[(C_2H_4)_2RhCl]_2$) and allene[6]; prior synthesis of the ligand 1,2,5,6,8-pentamethylenecyclodecane is thus unnecessary. This paper describes several new reactions of $C_{15}H_{20}RhCl$[(I)X=Cl] and related compounds.



(I)

EXPERIMENTAL

Microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Infrared spectra were taken in potassium bromide pellets and recorded on a Perkin–Elmer Model 621 spectrometer with grating optics. Proton NMR spectra were taken in the indicated solvents and recorded on a Varian HA-100 spectrometer at 100 Mc. Mass spectra were taken at 70 ev. on a Perkin–Elmer–Hitachi RMU-6 mass spectrometer with a chamber temperature of 220°C. Melting points were taken in capillaries and are uncorrected.

A nitrogen atmosphere was routinely provided for the following three operations: (1) Carrying out reactions; (2) Handling filtered solutions of organometallic compounds; (3) Admitting to evacuated vessels.

Materials

The complex of $C_{15}H_{20}RhCl$[(I)X=Cl] was prepared by reaction of $[(C_2H_4)_2RhCl]_2$ with allene in benzene solution according to the published procedure[6]. From 2.2 g (5.65 mmoles) of $[(C_2H_4)_2RhCl]_2$ we obtained 1.9 g (50% yield) of yellow $C_{15}H_{20}RhCl$, m.p. 220–225° (dec.) (lit.[6] m.p. 225–226°).

The other reagents used in this work were commercial products.

Preparation of $C_{15}H_{20}RhC_6F_5$

A solution of (pentafluorophenyl)lithium was prepared at −78° by brief stirring of 3 ml of commercial 1.6 *M* n-butyllithium (4.8 mmoles) in hexane with 0.5 g (3 mmoles) of pentafluorobenzene in 200 ml of anhydrous diethyl ether. This (pentafluorophenyl)lithium solution was kept at −78° while being treated with a solution of 0.4 g (1.2 mmoles) of $C_{15}H_{20}RhCl$ in a mixture of 50 ml of diethyl ether and 50 ml of benzene. The reaction mixture was then stirred at room temperature for 2 h. Solvent was then removed at 25°/40 mm. The residue was extracted with two 100 ml portions of benzene. The filtered benzene extracts were concentrated at ~25°/40 mm. Excess hexane was added to the concentrated benzene solution to give 0.28 g (50% yield) of yellow crystalline $C_{15}H_{20}RhC_6F_5$, m.p. 185–188° (dec.). (Found: C, 53.7; H, 4.6; F, 20.1. Mol. wt., 470 (osmometer in benzene). $C_{21}H_{20}F_5Rh$: calcd. C, 53.6; H, 4.3; F, 20.2%. Mol. wt. 470.)

Infrared spectrum (KBr Pellet). ν(CH) frequencies at 2987 (vw), 2924 (w), 2912 (w), 2866 (vw) cm^{-1}; ν(C=C) frequency at 1630 (m) cm^{-1}; other bands at 1600 (w), 1494 (s), 1461 (w), 1430 (s), 1414 (s), 1361 (w), 1319 (w), 1304 (w), 1268 (w), 1095 (vw), 1059 (m), 1042 (m), 997 (w), 945 (s), 932 (m), 896 (m), 805 (vw), 777 (vw), 745 (w), 727 (vw), 714 (vw), and 640 (vw) cm^{-1}.

Proton NMR spectrum (chloroform-d solution). Resonances at τ 4.70 (broad, width at half-height 12 Hz) and τ 4.92 (broad, width at half-height 12 Hz) assigned to the two different uncomplexed olefinic protons. Broad resonance at τ~5.8 (width at half-height 20 Hz) assigned to the four complexed olefinic protons in *anti*-positions relative to the metal atoms. Resonances at τ~6.8 (broad, width at half-height 12 Hz), τ 9.18 (doublet, *J* 3 Hz) and τ 9.26 (doublet, *J* 3 Hz) assigned to the four complexed olefinic protons in *anti*-positions relative to the metal atom. Broad resonance at τ 7.06 (width at half-height ~ 14 Hz) corresponding to one CH_2 group and another very broad resonance covering the range τ 7.2 to τ 7.5 corresponding to the other four CH_2 groups.

Preparation of $C_{15}H_{20}RhC_5H_5$

A solution of sodium cyclopentadienide was prepared from 0.4 g (16 mmoles) of sodium hydride and 6.0 ml (4.8 g,,72.5 mmoles) of monomeric cyclopentadiene in 100 ml of tetrahydrofuran (redistilled over $LiAlH_4$). This solution was treated with 1.0 g (3 mmoles) of $C_{15}H_{20}RhCl$. The reaction mixture was then stirred for 6 h at room temperature and then boiled under reflux for 8 h. Solvent was then removed at ~25°/40 mm. The residue was extracted with two 100 ml portions of benzene. The filtered benzene extracts were evaporated to dryness at ~25°/40 mm. A concentrated pentane solution of the oily residue was chromatographed on a 2×90 cm alumina column. The yellow band of the product was eluted with a 4/1 mixture of pentane and chloroform. Solvent was removed from this eluate at ~25°/40 mm. The resulting yellow oil was treated with 5 ml of pentane. The pentane solution was cooled in a −78° bath. Yellow crystals separated. These were removed by filtration and purified by sublimation at 130–140°/1–2 mm. onto a water-cooled probe to give 0.25 g (22% yield) of yellow $C_{15}H_{20}RhC_5H_5$, m.p. 38°. (Found: C, 65.6; H, 6.9. $C_{20}H_{25}Rh$ calcd.: C, 65.3; H, 6.8%.)

Infrared spectrum (KBr Pellet). ν(CH) frequencies at 3075 (w, br), 2965 (w, sh), 2095 (m, br), and 2855 (w, sh) cm^{-1}; ν(C=C) frequencies at 1625 (vw) and 1585 (w) cm^{-1}; other bands at 1438 (m), 1418 (m), 1098 (w), 1002 (w), 992 (w), 937 (w), 888 (s), 788 (s), 677 (vw), and 632 (vw) cm^{-1}.

Proton NMR spectrum. The proton NMR spectrum of $C_{15}H_{20}RhC_5H_5$ ($CDCl_3$ solution) was too complex to be readily described and so is depicted in Fig. 1.

Mass spectrum: The following rhodium-containing ions were observed (relative intensities given in parentheses): $C_{15}H_{20}RhC_5H_5^+$ (19), $C_{15}H_{20}Rh^+$ (100), $C_{15}H_{18}Rh^+$ (25), $C_{15}H_{16}Rh^+$ (12), $C_5H_5Rh^+$ (21), and Rh^+ (10). The following rhodium-free hydrocarbon ions of the type $C_mH_n^+$ were observed with a relative intensity of at least 10: $m=15, n=20$; $m=14, n=17$; $m=13, n=16$ and 15; $m=12, n=13$; $m=11, n=9$, 10, 11, 12, and 13; $m=10, n=8$, 9, 10, 11, 12 and 13; $m=9, n=7$, 8, 9, 10 and 11; $m=8$, $n=7$, 8 and 9; $m=7$, $n=7$; $m=6$, $n=5$, 6 and 7; $m=5$, $n=5$, 6 and 7; $m=4$, $n=3$, 4 and 5.

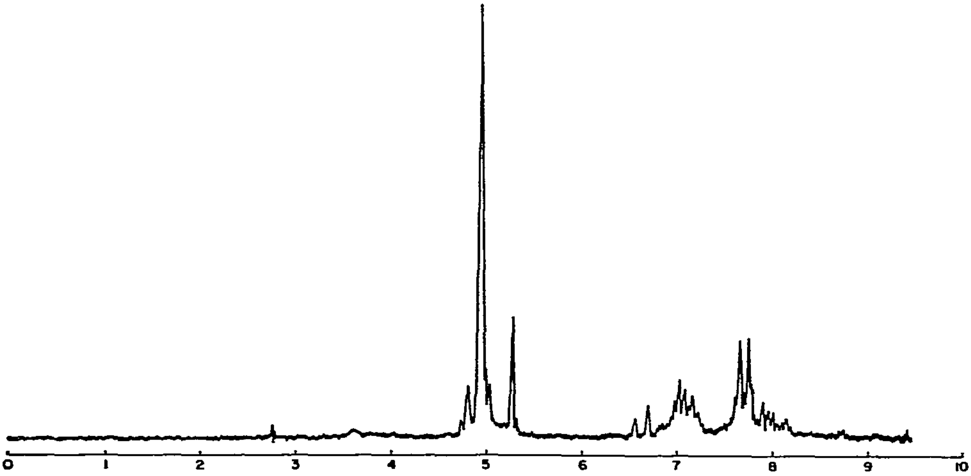


Fig. 1. Proton NMR spectrum of $C_{15}H_{20}RhC_5H_5$ in $CDCl_3$ solution.

Preparation of $C_{15}H_{20}RhSnCl_3$

A mixture of 0.3 g (0.89 mmoles) of $C_{15}H_{20}RhCl$, 0.17 g (0.89 mmoles) of stannous chloride, and 100 ml of diethyl ether was stirred for 20 h at room temperature. The reaction mixture was then kept at least overnight at −10°. The resulting precipitate was filtered and dried to give 0.22 g of yellow $C_{15}H_{20}RhSnCl_3$, m.p. 255–257° (dec.). An additional 0.08 g of $C_{15}H_{20}RhSnCl_3$ was obtained by evaporation of the filtrate. The total yield of $C_{15}H_{20}RhSnCl_3$ was therefore 0.30 g (64%). Attempted recrystallization of $C_{15}H_{20}RhSnCl_3$ resulted in decomposition. (Found: C, 33.3; H, 3.8; Cl, 20.2. $C_{15}H_{20}Cl_3RhSn$ calcd.: C, 34.1; H, 3.8; Cl, 20.1%.)

Infrared spectrum (KBr Pellet). ν(CH) frequencies at 2981 (vvw), 2930 (vw), 2904 (vw), and 2857 (vvw) cm^{-1}; ν(C=C) frequency at 1625 (w) cm^{-1}; other frequencies at 1500 (w), 1460 (m), 1408 (m), 1375 (vw), 1325 (w), 1310 (m), 1280 (vw), 1266 (vw), 1249 (vvw), 1205 (vw), 1159 (w), 1095 (w), 997 (w), 940 (w), 921 (m), 914 (m), 822 (w), 806 (w), 781 (w), 717 (w), and 640 (w) cm^{-1}.

Preparation of $[C_{15}H_{20}Rh][PF_6]$:

A mixture of 0.3 g (0.89 mmoles) of $C_{15}H_{20}RhCl$, 0.23 g (0.91 mmoles) of silver hexafluorophosphate (from Ozark–Mahoning, Inc., Tulsa, Oklahoma), and 20 ml of acetone was stirred for 6 h at room temperature. Solvent was then removed from the filtered reaction mixture at ~25°/40 mm. The residue was recrystallized from a mixture of ethanol and diethyl ether and washed with diethyl ether to give 0.25 g (63% yield) of yellow solid $[C_{15}H_{20}Rh][PF_6]$, m.p. 178–180° (dec.). (Found: C, 40.3; H, 4.6; F, 23.0. $C_{15}H_{20}F_6PRh$ calcd.: C, 40.2; H, 4.5; F, 25.4%.)

Infrared spectrum (KBr Pellet). ν(CH) frequencies at 3000 (vvw), 2960 (vw), 2931 (vw), and 2870 (vw) cm^{-1}; ν(C=C) frequency at 1624 (w) cm^{-1}; ν(PF) frequency at 836 (vs); other bands at 1683 (w), 1570 (vw), 1526 (vw), 1501 (vw), 1462 (m), 1406 (w), 1321 (vw), 1310 (vw), 1287 (vw), 1262 (vw), 1123 (vw), 1097 (vw), 1020 (vw), 931 (m), 736 (vw), 720 (vvw), 702 (vvw) and 637 (vw) cm^{-1}.

Proton NMR spectrum (acetone-d_6 solution). Resonances at τ 4.50 (singlet) and τ 4.70 (singlet) assigned to the two different uncomplexed olefinic protons. Resonances at τ 5.24 (singlet), τ 5.66 (singlet), τ 5.95 (singlet), and τ 6.44 (singlet) assigned to the four complexed olefinic protons in *anti*-positions relative to the metal atom. Resonances at τ 6.60 (doublet, J 3 Hz), 6.96 (singlet), 8.24 (singlet), and 8.51 (doublet, J 3 Hz) assigned to the four complexed olefinic protons in *syn*-positions relative to the metal atom. Very broad resonance at τ 5.9 corresponding to one CH_2 group and another very broad resonance covering the range τ 6.6 to 7.6 corresponding to the other four CH_2 groups.

Preparation of $[C_{15}H_{20}RhCO][PF_6]$:

(*a*). *By carbonylation of* $C_{15}H_{20}RhCl$. A solution of 0.3 g (0.89 mmoles) of $C_{15}H_{20}RhCl$ in 100 ml of boiling ethanol was treated with carbon monoxide at atmospheric pressure for 6 h. After cooling to room temperature solvent was removed at ~25°/40 mm. The residual oil exhibited terminal ν(CO) frequencies at 2070 (s) and 1990 (s) cm^{-1}. This oil was treated with ammonium hexafluorophosphate in aqueous acetone. The resulting precipitate was filtered, dried, and rerystallized from a mixture of ethanol and petroleum ether to give 0.24 g (57% yield) of yellow crystalline $[C_{15}H_{20}$-$RhCO][PF_6]$, m.p. 255–258° (dec.). (Found: C, 40.6; H, 4.2; F, 24.1. $C_{16}H_{20}F_6$-$OPRh$ calcd.: C, 40.3; H, 4.2; F, 23.9%.)

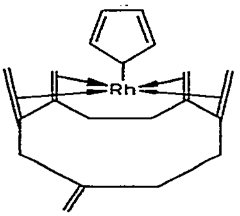
Infrared spectrum (KBr pellet). ν(CH) frequencies at 3097 (w), 3006 (w), 2992 (w), 2938 (w, br), and 2868 (vw) cm^{-1}; ν(CO) frequency at 2090 (vs) cm^{-1}; ν(C=C) frequency at 1628 (w) cm^{-1}; ν(PF) frequency at 840 (vs) cm^{-1}; other bands at 1536 (w), 1518 (w), 1476 (sh), 1466 (m), 1416 (vw), 1379 (w), 1348 (vw), 1337 (vw), 1324 (w), 1312 (w), 1294 (w), 1271 (vw), 1217 (w), 1169 (vvw), 1160 (vvw), 1120 (vvw), 1092 (vvw), 999 (vw), 990 (w), 982 (w), 973 (w), 964 (w), 953 (w), 941 (m), 930 (m), 878 (sh), 740 (vw), 728 (vw), 718 (w), 666 (vw), and 642 (vw) cm^{-1}.

(*b*). *By carbonylation of* $[C_{15}H_{20}Rh][PF_6]$. A solution of 0.5 g (1.12 mmoles) of $[C_{15}H_{20}Rh][PF_6]$ in 100 ml of boiling ethanol or tetrahydrofuran was treated with carbon monoxide at atmospheric pressure for 20 h. The reaction mixture was then filtered from some insoluble brown-black decomposition products. The yellow filtrate was then concentrated at ~25°/40 mm. Excess petroleum ether was then added to give 0.26 g (49% yield) of a yellow solid indicated to be primarily $[C_{15}H_{20}RhCO]$-$[PF_6]$ from its infrared spectrum.

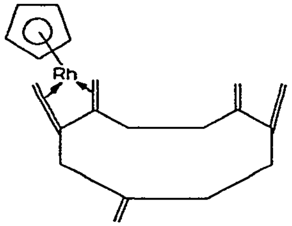
DISCUSSION

The reactions of (1,2,5,6,8-pentamethylenecyclodecane)rhodium(I) chloride, $C_{15}H_{20}RhCl[(I)X=Cl]$ with several reactive organometallic compounds were investigated in attempts to replace the chlorine atom in (I) with σ-bonded organic groups. Neither methylmagnesium bromide nor methyllithium gave tractable products when the reactions were carried out in diethyl ether solution. This suggests limited stability for the σ-methyl derivative $C_{15}H_{20}RhCH_3[(I)X=CH_3]$. In an attempt to prepare a more stable $C_{15}H_{20}RhR$ derivative with the R group σ-bonded to the rhodium atom through a carbon atom, the reaction between $C_{15}H_{20}RhCl$ and (pentafluorophenyl)lithium was investigated. This reaction gave the stable yellow crystalline pentafluorophenyl derivative $C_{15}H_{20}RhC_6F_5$ $[(I)\ X=C_6F_5]$. The proton NMR spectrum of the $C_{15}H_{20}$ ligand in $C_{15}H_{20}RhC_6F_5$ $[(I)X=C_6F_5]$ indicated that the allene pentamer unit had remained intact including the uncomplexed, carbon–carbon double bond. The pentafluorophenyl group therefore in $C_{15}H_{20}RhC_6H_5$ is directly bonded to the rhodium atom. The compound $C_{15}H_{20}RhC_6H_5$ appears to represent the first example where a transition metal–carbon σ-bond is surrounded exclusively with metal–olefin bonds. The existence and stability of $C_{15}H_{20}RhC_6F_5$ is a further demonstration of the very high stability of perfluoraryl derivatives of transition metals relative to other types of alkyl derivatives of transition metals[7].

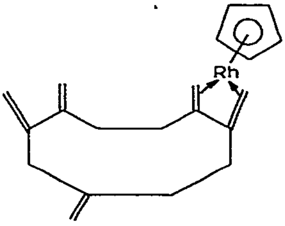
Some reactions of $C_{15}H_{20}RhCl$ $[(I)X=Cl]$ with unsaturated reactive organometallic compounds were also investigated. Allylmagnesium chloride gave a small quantity of an oily product from which crystals could not be isolated. Sodium cyclopentadienide reacted with $C_{15}H_{20}RhCl$ $[(I)\ X=Cl]$ to give a volatile waxy yellow solid of stoichiometry $C_{15}H_{20}RhC_5H_5$. This compound could either be (II) with a *monohapto*-cyclopentadienyl* ligand and an *octahapto*-1,2,5,6,8-pentamethylenecyclodecane ligand or (III)** with a *pentahapto*-cyclopentadienyl ligand and a *tetrahapto*-1,2,5,6,8-pentamethylenecyclodecane ligand if one assumes that the rhodium atom in $C_{15}H_{20}RhC_5H_5$ has the favored 18-electron rate gas configuration[2]. In an attempt to distinguish between structures (II) and (III) the proton NMR spectrum of $C_{15}H_{20}RhC_5H_5$ was investigated (Fig. 1). This NMR spectrum was temperature independent up to 90°. In this proton NMR spectrum a sharp peak at τ 4.95 arising from the five equivalent cyclopentadienyl protons could be clearly discerned. This observation alone is not sufficient to demonstrate unambiguously the presence of a pentahapto-cyclopentadienyl ring in $C_{15}H_{20}RhC_5H_5$ since a fluxional process[9] could make the



(II)



(IIIa)



(IIIb)

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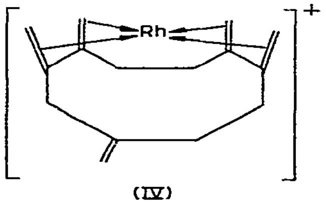
* For a summary of the "*hapto*" system of nomenclature of organometallic compounds, see ref. 8.

** Actually two difficultly distinguishable isomers (IIIa) and (IIIb) are possible.

three types of chemically non-equivalent protons in a *monohapto*-cyclopentadienyl ring appear equivalent on the NMR time scale (*e.g.* $C_5H_5Fe(CO)_2C_5H_5$[10]). However, the portion of the NMR spectrum of $C_{15}H_{20}RhC_5H_5$ arising from the protons of the $C_{15}H_{20}$ ligand, although too complex for precise assignment for each peak (see Fig. 1), suggests structure (III) for $C_{15}H_{20}RhC_5H_5$ with a *pentahapto*-cyclopentadienyl ligand and a *tetrahapto*-1,2,5,6,8-pentamethylenecyclodecane ligand rather than structure (II) with a *monohapto*-cyclopentadienyl ligand and an *octahapto*-1,2,5,6,8-pentamethylenecyclodecane ligand. The resonances in the NMR spectrum of $C_{15}H_{20}RhC_5H_5$(Fig. 1) appear in two distinctly separated clusters. The lower field cluster covers the range τ 4.5–5.5 and can be assigned to the uncomplexed olefinic protons and the five cyclopentadienyl protons whether the cyclopentadienyl ring is *pentahapto* or fluxional *monohapto* (see above). The higher field cluster covers the range τ 6.2–8.2 and can be assigned to the complexed olefinic protons and the ten methylene protons. The assignments of the complexed and uncomplexed olefinic protons in the NMR spectrum of $C_{15}H_{20}RhC_5H_5$ are based on the reported[6] chemical shifts for the various type of olefinic protons in $C_{15}H_{20}RhCl$ [(I) X=Cl]. The relative intensity ratio of the high field cluster of peaks to the low field cluster of peaks was measured by integration and found to be 1.32 ($CDCl_3$ solution), 1.26 (C_6D_6solution), and 1.27 (C_6F_6 solution) as compared with an expected value of 1.27 (14/11) for structure(III) and 2.57 (18/7) for structure(II). This NMR measurement thus suggests structure(III) rather than structure(II) for $C_{15}H_{20}RhC_5H_5$. This provides a further indication of the well-known tendency for a cyclopentadienyl ring to bond to transition metals through all five carbon atoms whenever possible. Sodium cyclopentadienide thus appears capable of displacing two of the four rhodium–olefin bonds in $C_{15}H_{20}RhCl$ [(I) X=Cl].

Certain compounds with transition metal–halogen bonds including the norbornadiene–rhodium derivative $[C_7H_8RhCl]_2$ react with stannous chloride to form $SnCl_3$ derivatives with transition metal–tin bonds[11]. The rhodium derivative $C_{15}H_{20}RhCl$ [(I) X=Cl] also reacted with stannous chloride in this manner to give the yellow trichlorotin derivative $C_{15}H_{20}RhSnCl_3$ apparently with structure [(I) X=$SnCl_3$] containing a rhodium–tin bond. However, detailed studies on $C_{15}H_{20}RhSnCl_3$ were prevented by its instability in solution apparently with respect to reversion to $C_{15}H_{20}RhCl$ and stannous chloride.

The compound $C_{15}H_{20}RhX$ [(I) X=Cl] is a five-coordinate 18-electron rhodium(I) derivative. Square planar four-coordinate 16-electron rhodium(I) derivatives are also very stable in many cases. The four-coordinate 16-electron rhodium(I) cation $[C_{15}H_{20}Rh]^+$ (IV) was prepared as its yellow hexafluorophosphate salt by removal of chlorine from $C_{15}H_{20}RhCl$ [(I) X=Cl] through reaction with an equimolar quantity of silver hexafluorophosphate. The proton NMR spectrum of $[C_{15}H_{20}Rh][PF_6]$ was similar to that of $C_{15}H_{20}RhCl$ [(I)X=Cl] except for the relatively small chemical



(IV)

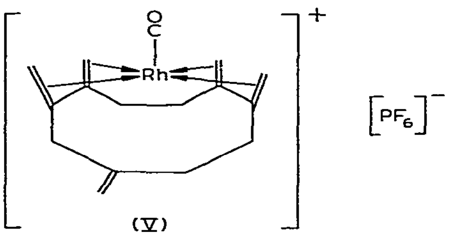
shift changes expected from the change in the rhodium stereochemistry. This confirms that the 1,2,5,6,8-pentamethylenecyclodecane ligand remains intact upon conversion of $C_{15}H_{20}RhCl$ [(I) X=Cl] to $[C_{15}H_{20}Rh]^+$ (IV) and also that the same number of carbon–carbon double bonds are complexed to the rhodium atom in both $C_{15}H_{20}RhCl$ and $[C_{15}H_{20}Rh]^+$.

The ion $[C_{15}H_{20}Rh]^+$, besides forming stable isolable salts, also appears to be a favored ion in the mass spectra of rhodium complexes of 1,2,5,6,8-pentamethylenecyclodecane. The one compound in this study which was volatile enough for mass spectrometry in the available spectrometer was the π-cyclopentadienyl derivative $C_{15}H_{20}RhC_5H_5$ (III). In the mass spectrum of $C_{15}H_{20}RhC_5H_5$ (III) the ion $C_{15}H_{20}Rh^+$ is at least four times more abundant than any other ion containing rhodium including the molecular ion. Thus in the mass spectrum of $C_{15}H_{20}RhC_5H_5$ (III) the relative abundance of the ion $C_{15}H_{20}Rh^+$ which results from cleavage of the rhodium–cyclopentadienyl bond is about five times that of the ion $C_5H_5Rh^+$ which results from the cleavage of the rhodium–$C_{15}H_{20}$ bond. Furthermore the only metastable ion of appreciable intensity in the mass spectrum of $C_{15}H_{20}RhC_5H_5$ (III) occurs at *m/e* 250 corresponding to cyclopentadienyl loss from the molecular ion according to the following process ($303^2/368=249.5$):

$$C_{15}H_{20}RhC_5H_5^+ \rightarrow C_{15}H_{20}Rh^+ + C_5H_5$$

The high abundance of $C_{15}H_{20}Rh^+$ relative to $C_5H_5Rh^+$ in the mass spectrum of $C_{15}H_{20}RhC_5H_5$ (III) may be attributed to the fact that the rhodium(I) atom in $C_5H_5Rh^+$ cannot have more than 14 outer electrons.

The 16-electron cation $[C_{15}H_{20}Rh]^+$ can potentially add another ligand to form an 18-electron cation $[C_{15}H_{20}Rh]^+$ (L=Lewis base ligand, etc.). Thus $[C_{15}H_{20}Rh][PF_6]$ reacts with carbon monoxide at ~70° to give the yellow 18-electron cation $[C_{15}H_{20}RhCO]^+$ (V) which can be isolated as its hexafluorophosphate salt $[C_{15}H_{20}RhCO][PF_6]$. The cation $[C_{15}H_{20}RhCO]^+$ (V) exhibits the expected single ν(CO) frequency consistent with the presence of one carbonyl group. A more convenient preparation of the salt $[C_{15}H_{20}RhCO][PF_6]$ (V) utilizes the reaction of $C_{15}H_{20}RhCl$ [(I) X=Cl] with carbon monoxide at atmospheric pressure followed by treatment with ammonium hexafluorophosphate. The intermediate product obtained from $C_{15}H_{20}RhCl$ [(I) X=Cl] and carbon monoxide in boiling ethanol prior to addition of ammonium hexafluorophosphate was an oil which exhibited two ν(CO) frequencies (2070 and 1990 cm^{-1}) of about equal relative intensities. This suggests the presence of a dicarbonyl intermediate such as $[C_{15}H_{20}Rh(CO)_2]^+$ or $C_{15}H_{20}Rh(CO)_2Cl$. Such dicarbonyl intermediates must have the 1,2,5,6,8-pentamethylenecyclodecane ($C_{15}H_{20}$) unit acting as a bidentate or tridentate ligand rather than as a tetradentate ligand as in $C_{15}H_{20}RhCl$ [(I)X=Cl]. This indicates that carbon monoxide under relatively mild conditions can displace at least one of the four coordinated carbon–carbon double bonds in the rhodium(I) complex $C_{15}H_{20}RhCl$ [(I) X=Cl]. However, the instability of the elusive dicarbonyl intermediate as demonstrated by its conversion to the monocarbonyl $[C_{15}H_{20}RhCO][PF_6]$ when treated with ammonium hexafluorophosphate in aqueous acetone at room temperature indicates that the carbon–carbon double bond in the $C_{15}H_{20}$ ligand which was released from bonding to the rhodium during the reaction with carbon monoxide can, under mild conditions, displace a carbonyl group.


(V)

Several other reactions of $C_{15}H_{20}RhCl$ [(I) X=Cl] were investigated. Treatment of $C_{15}H_{20}RhCl$ [(I) X=Cl] with ethylene at atmospheric pressure in boiling ethanol gave no identifiable products. Instead about 77% of the $C_{15}H_{20}RhCl$ was recovered. Treatment of $C_{15}H_{20}RhCl$ [(I) X=Cl] with hydrogen at atmospheric pressure in tetrahydrofuran solution likewise resulted in high recovery of unchanged $C_{15}H_{20}RhCl$ [(I) X=Cl]. No tractable rhodium–hydrogen compounds could be obtained from this reaction. Likewise no rhodium–hydrogen compounds were obtained when $C_{15}H_{20}RhCl$ [(I) X=Cl] was treated with either lithium aluminum hydride in diethyl ether at room temperature, tetramethylammonium octahydrotriborate in boiling tetrahydrofuran, or sodium cyanotrihydroborate in ethanol at room temperature. Attempted formation of a rhodium–iron bond by reaction of $C_{15}H_{20}RhCl$ [(I) X=Cl] with $NaFe(CO)_2C_5H_5$ gave $[C_5H_5Fe(CO)_2]_2$ as the only identifiable product. Attempted transfer of the $C_{15}H_{20}$ ligand from rhodium to iron by heating $C_{15}H_{20}RhCl$ with $Fe(CO)_5$ in boiling xylene gave relatively small amounts of oils which could not be identified.

ACKNOWLEDGEMENT

We are indebted to the National Science Foundation for partial support of this work under Grant GP-9662.

REFERENCES

1 R. B. King and P. N. Kapoor, *Inorg. Chem.*, 10 (1971) in press.
2 R. B. King, *Advan. Chem. Ser.*, 62 (1967) 203.
3 L. Porri, A. Lionetti, G. Allegra and A. Immirzi, *Chem. Commun.*, (1965) 336; L. Porri and A. Lionetti, *J. Organometal. Chem.*, 6 (1966) 422.
4 A. E. Martell and M. Calvin, *Chemistry of the Metal Chelate Compounds*, Prentice-Hall, New York, 1952.
5 M. A. Bennett and J. D. Saxby, *Inorg. Chem.*, 7 (1968) 321.
6 S. Otsuka, K. Tani and A. Nakamura, *J. Chem. Soc. A*, (1969) 1404.
7 R. D. Chambers and T. Chivers, *Organometal. Chem. Rev.*, 1 (1966) 279.
8 F. A. Cotton, *J. Amer. Chem. Soc.*, 90 (1968) 6230.
9 F. A. Cotton, *Accounts Chem. Res.*, 1 (1968) 257.
10 M. J. Bennett, F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard and S. M. Morehouse, *J. Amer. Chem. Soc.*, 88 (1966) 4371.
11 J. F. Young, R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, (1964) 5176.