646. *Norbornadiene–Metal Complexes and Some Related Compounds.*

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Norbornadiene has given diolefin complexes of silver(I), copper(I), palladium(II), platinum(II), rhodium(I), and ruthenium(II), the last being the first reported olefin complex of ruthenium. The ruthenium–diolefin complex, $C_7H_8RuX_2$ is polymeric with a halogen-bridged structure. Compounds of the type $C_7H_8(p\text{-tol})_2RuX_2$ and py_4RuX_2 are obtained from the polymeric olefin complex with *p*-toluidine and pyridine, respectively. Rhodium(I) complexes of cyclo-octatetraene, the maleic anhydride adduct of cyclo-octatetraene, and the cyclo-octatetraene–(dimethyl acetylenedicarboxylate) adduct, have been made; they are binuclear with the general formula $(diene)_2Rh_2Cl_2$.

IN this paper we report the formation of a series of metal–olefin complexes obtained from the hydrocarbon norbornadiene (bicyclo[2,2,1]hepta-2,5-diene) (I). The most stable olefin co-ordination complexes previously known have been those formed by cyclo-octa-1,5-diene,[1] which was used by Chatt and his co-workers to determine the limits of olefin–metal complex formation in the Periodic Table. The farthest point reached to the left of the Table by these workers was rhodium. It was reported that iridium, ruthenium, and osmium did not form complexes with the octadiene.[1] We have now been able to move one Group further to the left of the Periodic Table by the formation of the norbornadiene-ruthenium dihalides; a norbornadiene–iron compound of a different type, $C_7H_8Fe(CO)_3$, has also been prepared [2] and will be described in more detail subsequently. Although no unconjugated olefin complex of a metal to the left of the iron Group has been made directly from the olefin, the rhenium–olefin complexes, $\pi\text{-}C_5H_5Re(CO)_2C_5H_6$ and $\pi\text{-}C_5H_5Re(CO)_2C_5H_8$, have been obtained indirectly.[3]

With silver nitrate, norbornadiene produced the compound $C_7H_8(AgNO_3)_2$ as white crystals; this is in contrast to the 1 : 1 metal–diene complex formed by cyclo-octa-1,5-diene.[4] Recently, however, it was reported [5] that norbornadiene forms a 1 : 1 silver

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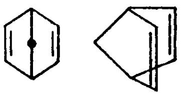
[1] Chatt and Venanzi, *J.*, 1957, 4735, and papers quoted therein.
[2] Burton, Green, Abel, and Wilkinson, *Chem. and Ind.*, 1958, 1592.
[3] Green and Wilkinson, *J.*, 1958, 4314.
[4] Jones, *J.*, 1954, 312.
[5] Traynham and Olechowski, *J. Amer. Chem. Soc.*, 1959, **81**, 571.

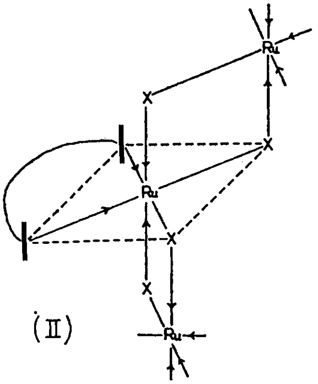
complex; the product was not crystallised in this case. It appears that the stoicheiometry of the silver nitrate–cyclopolyolefin compounds may vary considerably, depending on the conditions of preparation.[6] Anhydrous cupric bromide and norbornadiene in ethanol formed the Cu(I) compound, $C_7H_8(CuBr)_2$, analogous to the above silver nitrate complex.

The norbornadiene complexes of rhodium(I), $(C_7H_8)_2Rh_2Cl_2$, palladium(II), $C_7H_8PdCl_2$, and platinum(II), $C_7H_8PtCl_2$, appear to be analogous to the corresponding compounds of cyclo-octa-1,5-diene.[1,7,8] Thus, it is reasonable to assume that the metal in these compounds has a planar 4-co-ordinate dsp^2-hybridized state. The compounds are insoluble in water, but soluble in chloroform, acetic acid, and other organic solvents.

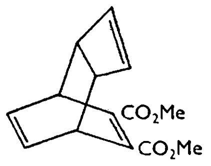
Norbornadieneruthenium dichloride, $C_7H_8RuCl_2$, was made by direct reaction between ruthenium trichloride and the hydrocarbon in ethanol; the corresponding bromide was formed similarly. If, in these compounds, the metal was regarded as having a co-ordination number of four, both the planar (dsp^2) and the tetrahedral (sp^3) form would have to be paramagnetic. The compounds are, however, diamagnetic, and in view of the virtually unknown co-ordination number of four for ruthenium, the metal undoubtedly attains its usual co-ordination number of six by the formation of the halogen-bridged structure (II; X = halogen). This structure resembles that proposed by Irving[9] for ruthenium carbonyl iodide, in having halogen bridges; although the relative disposition of the carbonyl groups was not explicitly stated, the diagram given indicates a *trans*-position for the two carbonyl groups. The infrared spectrum of the compound shows two very strong C–O stretching modes at 1995 and 2050 cm.$^{-1}$, so that a *cis*-configuration appears more likely, although solid-state interaction in the *trans*-form, which could lead to splitting of the expected single frequency, cannot be rigorously excluded. However, in the above diolefin complex, the olefin groups must necessarily be mutually *cis*. This results in a " curling " spiral chain structure for $C_7H_8RuX_2$. Such a spiral chain structure with *cis*-carbonyl groups is also a more likely alternative structure for the carbonyl iodide. The virtual insolubility of $C_7H_8RuX_2$, as well as $(CO)_2RuX_2$, in all solvents supports the polymeric structure for these compounds.



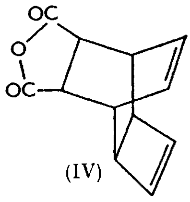
(I)



(II)



(III)



(IV)

p-Toluidine caused fission of the halogen bridge in $[C_7H_8RuX_2]_n$ to give the corresponding bis-*p*-toluidinenorbornadieneruthenium dihalides:

$$(C_7H_8RuX_2)_n + 2n(p\text{-tol}) = nC_7H_8(p\text{-tol})_2RuX_2$$

Pyridine not only caused fission of the halogen bridge in the diolefin polymer but also displaced the diolefin to give the monomeric tetrapyridineruthenium dihalides; other reactions of this type will be reported later.

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[6] Cope and Hochstein, *J. Amer. Chem. Soc.*, 1950, **72**, 2515.

[7] Chatt, Vallarino, and Venanzi, *J.*, 1957, 2496.

[8] *Idem*, *J.*, 1957, 3413.

[9] Irving, *J.*, 1956, 2879.

Rhodium trichloride in ethanol solution has proved particularly reactive towards compounds having a chelating diolefin group, and compounds of general formula $L_2Rh_2Cl_2$ have been isolated where L is cyclo-octatetraene, the cyclo-octatetraene–(dimethyl acetylenedicarboxylate) adduct (III) and cyclo-octatetraene–maleic anhydride adduct (IV). The rhodium chloride complexes of the first two of these have been shown to be dimeric, but the low solubility of the other product prevented a direct determination. These three compounds may be regarded as analogous to the octa-1,5-diene and norbornadiene complexes of rhodium. All three compounds are stable in the crystalline form, and in solution, despite a previous report[1] that cyclo-octatetraenerhodium chloride was too unstable to be purified.

It is interesting that in the adduct (III) there are three olefinic bonds and it is not possible at this stage to say definitely which pair is being used as a chelating diolefin. This problem is however being investigated as part of a programme of nuclear magnetic resonance studies on the above and other olefin complexes, results of which will be communicated later.

We may note finally that norbornadiene is the only chelating diolefin known so far which gives complexes with the elements at the heavy ends of the transitional series as well as with iron and ruthenium. Whilst norbornadiene has been shown[10] to behave as a quasi-conjugated system, undergoing, for example, the Diels–Alder addition with maleic anhydride, it is not certain yet whether this behaviour is essential for binding to iron or ruthenium although only conjugated olefins have previously been known to form complexes with iron.[11] Indeed, the nuclear magnetic resonance spectra of the norbornadiene–iron and -rhodium compounds[12] do not show the separation of the olefinic proton resonances into high- and low-field groups observed for conjugated olefin–metal complexes.[12] The distance between the double bonds in the diolefins may be the important factor, and scale models show the distance in norbornadiene to be about 10% shorter (2·5 Å) than in cyclo-octa-1,5-diene (2·8 Å); this shortening would obviously allow better overlap between the metal hybrid orbitals and the π-electron density in the olefin.

EXPERIMENTAL

Microanalyses and molecular-weight measurements were by the Microanalytical Laboratory, Imperial College. Magnetic measurements were made by the Gouy method.

Norbornadienedi(silver Nitrate).—Silver nitrate (1·36 g.) in water (10 c.c.) was added to the hydrocarbon (3 ml.) and shaken for 5 min. The white solid complex was filtered off and recrystallised from ethanol, to give the pure *product* (0·95 g.) [Found: C, 19·4; H, 2·4; Ag, 50·2. $C_7H_8(AgNO_3)_2$ requires C, 19·5; H, 1·9; Ag, 50·0%]. The white crystals decompose in water, giving a strong smell of norbornadiene; they also decompose when kept in the air or warmed. The complex is soluble in warm methanol, ethanol, carbon tetrachloride, chloroform, and benzene but is almost insoluble in acetone, ether, and light petroleum.

Norbornadienedi(cuprous Bromide).—Anhydrous cupric bromide (2·6 g.) in ethanol 30 c.c.) was shaken for 5 min. with norbornadiene (5 c.c.). After the white crystalline product had been removed by filtration it was washed with ethanol (5 c.c.) and ether (5 c.c.). *Norbornadienedi(cuprous bromide)* (1·4 g.) [Found: C, 19·8; H, 2·6; Cu, 32·8. $C_7H_8(CuBr)_2$ requires C, 22·2; H, 2·1; Cu, 33·5%] remained as fine white crystals which slowly become green in air. The complex readily lost norbornadiene at reduced pressure to leave cuprous bromide, and was decomposed in water to give cuprous oxide. It is practically insoluble in all common organic solvents.

Although the analytical figures are not satisfactory in spite of the formation of well-defined crystals, it may be noted that many other copper–olefin complexes have been reported to be unstable and in some cases analyses for carbon and hydrogen have not even been attempted (cf. ref. 13).

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[10] Ullman, *Chem. and Ind.*, 1958, 1173.

[11] Hallam and Pauson, *J.*, 1958, 642.

[12] Green, Pratt, and Wilkinson, *J.*, 1959, in the press.

[13] Slade and Jonassen, *J. Amer. Chem. Soc.*, 1957, **79**, 1277.

Interaction of Platinic Chloride and Norbornadiene.—The chloride (1 g.) in glacial acetic acid (10 c.c.) was shaken for 15 min. with norbornadiene (2 c.c.). The brown solid was filtered off and a further quantity obtained by addition of light petroleum to the mother-liquor. Recrystallization from acetic acid gave *norbornadieneplatinum dichloride* (0·4 g.) (Found: C, 23·8; H, 2·4; Pt, 54·6; Cl, 19·0. $C_7H_8PtCl_2$ requires C, 23·5; H, 2·3; Pt, 54·5; Cl, 19·8%) as fine white crystals, decomp. 230—280°, somewhat soluble in acetic acid, chloroform, and acetone.

Norbornadienepalladium Dichloride.—Dibenzonitrilepalladium dichloride[14] (1·1 g.) in chloroform (35 c.c.) was shaken with norbornadiene (4 c.c.) and set aside for 1 hr. The yellow deposit was filtered off and washed with chloroform and light petroleum. After recrystallization from acetic acid, the *product* was washed with methanol and acetone and dried in a vacuum. It formed yellow needles (0·58 g.), decomp. 190—200° (Found: C, 31·4; H, 3·6. $C_7H_8PdCl_2$ requires C, 31·2; H, 3·0%).

Norbornadieneruthenium Dichloride.—Ruthenium "trichloride" (1·03 g.) (commercial mixture of hydrated tri- and tetra-chloride) was dissolved in ethanol (40 c.c.), and the solution was centrifuged to remove insoluble material. The red-brown solution was shaken with norbornadiene (4 c.c.) and kept for 25 hr. The red product was washed repeatedly with acetone to remove ruthenium chlorides. The final *product* (0·6 g.) (Found: C, 31·6; H, 3·9; Cl, 27·5. $C_7H_8RuCl_2$ requires C, 31·8; H, 3·1; Cl, 26·8%) was diamagnetic and insoluble in water and all organic solvents.

Norbornadieneruthenium Dibromide.—Ruthenium "trichloride" (1·1 g.) was dissolved in acetone (40 c.c.), and insoluble material removed as above. Then lithium bromide (4 g.) was added and the solution was filtered and added to norbornadiene (4 c.c.) and set aside for 24 hr. The precipitated complex, after repeated washing with acetone, was dried in a vacuum, to give the pure *product* (0·6 g.) (Found: C, 23·2; H, 2·8. $C_7H_8RuBr_2$ requires C, 23·8; H, 2·3%) as a dark brown solid insoluble in all solvents.

Interaction of Norbornadieneruthenium Dichloride and Pyridine.—The dichloride (0·39 g.) in pyridine (15 c.c.) was heated at 120° for 45 min. Cooling the resultant red solution gave red crystals. Recrystallization from chloroform–light petroleum gave pure tetrapyridineruthenium dichloride (0·3 g.), m. p. 220—224° (decomp.) [Found: C, 49·4; H, 4·3; N, 11·4; Cl, 14·8%; *M*, 487 (ebullioscopic in benzene). Calc. for $C_{20}H_{20}Cl_2N_4Ru$: C, 49·1; H, 4·3; N, 11·5; Cl, 14·5%; *M*, 489].

Interaction of Norbornadieneruthenium Dihalides and p-*Toluidine.*—The dichloride (0·29 g.) was fused with *p*-toluidine (0·8 g.) and kept at 100° for 30 min. After being cooled, the red solid residue was washed with ether and dichloromethane, to leave yellow crystals which after vacuum-drying gave *norbornadienedi-*(p-*toluidine*)*ruthenium dichloride* (0·2 g.), decomp. >80° (Found: C, 53·1; H, 5·4; N, 6·2; Cl, 14·7. $C_{21}H_{26}N_2Cl_2Ru$ requires C, 52·6; H, 5·5; N, 5·9; Cl, 14·8%), soluble in chloroform.

In a similar manner *norbornadienedi-*(p-*toluidine*)*ruthenium dibromide*, decomp. >80° (Found: C, 45·0; H, 5·1; N, 4·9; Br, 27·9. $C_{21}H_{26}N_2Br_2Ru$ requires C, 44·4; H, 4·6; N, 4·9; Br, 28·2%), was prepared from $C_7H_8RuBr_2$ and *p*-toluidine.

Cyclo-octatetraenerhodium(I) *Chloride.*—Rhodium "trichloride" (1·4 g.) and cyclo-octatetraene (5 c.c.) in ethanol (50 c.c.) were kept at room temperature for 1 month. The fine orange crystals deposited were washed with ethanol and ether and dried in a vacuum, to leave pure *cyclo-octatetraenerhodium chloride* (0·2 g.), m. p. 140—145° (decomp.) [Found: C, 40·0; H, 3·9; Cl, 13·9%; *M*, 476 (ebullioscopic in benzene). $(C_8H_8RhCl)_2$ requires C, 39·6; H, 3·3; Cl, 14·6%; *M*, 485]. The complex is easily soluble in benzene, chloroform, and methylene dichloride to give yellow solutions which do not noticeably decompose when warmed; it is insoluble in light petroleum, ether, and ethanol.

Norbornadienerhodium(I) *Chloride.*—Rhodium trichloride (0·7 g.) and norbornadiene (2 c.c.) in aqueous ethanol (10 c.c.) were shaken together for 2 days. The yellow deposit was recrystallized from hot chloroform–light petroleum, to give pure *norbornadienerhodium chloride* (0·62 g.), decomp. 240° [Found: C, 37·3; H, 3·7; Rh, 45·3; Cl, 15·5%; *M*, 481 (ebullioscopic in benzene). $(C_7H_8RhCl)_2$ requires C, 36·5; H, 3·5; Rh, 44·6; Cl, 15·4%; *M*, 462], as fine yellow crystals, soluble in chloroform and benzene, but almost insoluble in ether and light petroleum.

Interaction of the Maleic Anhydride Adduct of Cyclo-octatetraene with Rhodium Trichloride.—The adduct (tricyclo[4,2,2,$0^{2,5}$]deca-3,9-diene-7,8-dicarboxylic anhydride) (0·75 g.) and trichloride (0·5 g.) in ethanol (25 c.c.) were heated at 70° for 2 hr. The yellow crystals deposited

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[14] Kharasch, Seyler, and Mayo, *J. Amer. Chem. Soc.*, 1938, **60**, 882.

were washed with alcohol and ether and dried in a vacuum, to leave *adduct–rhodium*(I) *chloride* (0·35 g.), decomp. 190° (Found: C, 42·0; H, 4·0; O, 14·7. $C_{12}H_8O_3RhCl$ requires C, 42·3; H, 3·0; O, 14·1%). Although direct measurement of the molecular weight of this compound was not possible owing to its low solubility, its diamagnetism suggests the dimeric structure analogous to all the other diolefin–rhodium chlorides described.

Interaction of Cyclo-octatetraene–(Dimethyl Acetylenedicarboxylate) Adduct and Rhodium Trichloride.—The adduct (dimethyl tricyclo[4,2,2,$0^{2,5}$]deca-3,7,9-triene-7,8-dicarboxylate) (1 g.) and trichloride (1 g.) in ethanol (10 c.c.) were heated at 70° for 1 hr. After cooling, the green-yellow crystals deposited were washed with cold alcohol and ether, and dried in a vacuum, to leave pale-green crystals of the *adduct–rhodium*(I) *chloride* [Found: C, 43·5; H, 3·9; Rh, 27·3; Cl, 9·4; O, 16·5%; *M*, 748 (ebullioscopic in benzene). $(C_{14}H_{14}O_4RhCl)_2$ requires C, 43·6; H, 3·6; Rh, 26·8; Cl, 9·4; O, 16·6%; *M*, 770], which are soluble in chloroform and benzene but only very slightly soluble in ether and light petroleum.

Infrared Spectra.—Spectra were measured on a Perkin-Elmer Model 21 spectrophotometer.

Norbornadiene in CCl_4 *and* CS_2: 3080(s), 2960(vs), 2880(s), 1646(m), 1452(ms), 1335(ms), 1310(vs), 1271(m), 1229(s), 1206(s), 1150(s), 1105(ms), 1063(m), 1016(m), 1016(m), 935(s), 911(s), 885(sh), 870(vs), 795(sh), 745(sh), 715(vs), 650(s).

$(C_7H_8)_2Rh_2Cl_2$ *in* CS_2: 3060(m), 3000(m), 2960(m), 2920(m), 2855(m), 1307(s), 1171(m), 1157(w), 1068(w), 1029(w), 995(w), 932(m) 882(m), 721(w), 680(s), 630(s).

$C_7H_8PtCl_2$ *in Nujol and hexachlorobutadiene mulls*: 3060(ms), 2930(w), 2880(w), 1436(m), 1412(w), 1371(sh), 1315—1310(split peak, s), 1262(vw), 1250(vw), 1187(m), 1162(vw), 1120—1025(vw, broad), 985(m), 978(m), 954(w), 939(w), 909(w), 880(vw), 833(vw), 822(w), 800(w), 775(w), 720(s, broad, rising).

$C_7H_8PdCl_2$ *in Nujol mull* (3000 $cm.^{-1}$ region omitted): 1410(m), 1305(m), 1230(w), 1180(m), 1160—1108(broad, w), 970(m), 941(m), 900(m), 880(w), 828(w), 797(sh), 792(m), 765(w), 718(w).

$C_7H_8,2AgNO_3$ *in Nujol and hexachlorobutadiene mulls*: 3020(w), 2960(w), 2885(w), 1470(m), 1385(v, broad, s), 1325(s), 1310(s), 1310(s), 1243(m), 1189(m), 1046(m), 1014(w), 969(m), 950(vw), 929(m), 890(w), 877(w), 808(m), 795(w), 790(m), 760(w), 725(ms).

$C_7H_8,2CuBr$ *in Nujol and hexachlorobutadiene mulls*: 3027(vw), 3000(vw), 2930(m), 2860(w), 1471(w), 1453(m), 1310(ms), 1265(w), 1245(vw), 1234(w), 1180—1080(broad,w), 1050(vw), 993(m), 976(m), 950(w), 938(w), 918(ms), 889(w), 867(w), 777(w), 765(w), 739(m), 719(m).

$C_7H_8RuCl_2$ *in Nujol and hexachlorobutadiene mulls*: 3098(w), 3098(w), 3025(m), 2975(sh), 2940(m), flat shoulder from 2863 to 2900, 1420(vw), 1409 (vw), 1310(m), 1258(vw), 1240(vw), 1180(w), 1160(w), 1085(w), 1035(w), 1000(vw), 941(w), 888(w), 863(w), 805(w), 779(w).

$C_7H_8RuBr_2$ *in Nujol and hexachlorobutadiene mulls*: 3025(w), 2960(m), 2915(vw), 2880(m), 1438(w), 1410(m), 1397(m), 1301(s), 1258(vw), 1225(vw), 1170(m), 1150(sh), 1078(w), 1025(vw), 935(w), 884(w), 858(w), 800(m), 775(m), 718(m).

$C_7H_8Ru(p\text{-tol})_2Cl_2$ *in Nujol mull below* 1400 *cm.*$^{-1}$ *only*: 1305(m), 1179(m), 1118(s), 1105(sh), 1040(w), 946(m), 840(m), 816(s), 799(m), 713(m).

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