COMPLEXES OF BICYCLO [3.3.1]NONA-2,6-DIENE WITH PALLADIUM(II), PLATINUM(II) AND RHODIUM(I)

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SUMMARY

   Complexes of bicyclo[3.3.1]nona-2,6-diene with formulae (diene)$PdCl_2$, (diene)$PtCl_2$, and [(diene)RhCl]$_2$ have been prepared and characterised. PMR and mass spectra are discussed.

INTRODUCTION

   As part of a programme designed to seek parallels between reaction mechanisms in organometallic chemistry and those of catalytic processes at metal surfaces, we have prepared molecular complexes having a suitable hydrocarbon ligand. This communication reports the preparation and physical characteristics of three complexes of bicyclo[3.3.1]nona-2,6-diene with, respectively, Pd[II], Pt[II] and Rh[I].

EXPERIMENTAL

   PMR spectra were recorded on a Perkin–Elmer R12 spectrometer with TMS as internal standard. Mass spectra are at 70 eV with a direct inlet system. M.p.'s are in air and are uncorrected. Bicyclo[3.3.1]nona-2,6-diene was prepared by the decomposition of the bis(tosylhydrazone) of bicyclo[3.3.1]nona-2,6-dione.

Bicyclo[3.3.1]nona-2,6-dione (I)
   This compound prepared by the method of Schaeffer and Honig[1] was purified by sublimation (3 mm, 120° to yield white crystals (83 %) which were recrystallised from benzene: m.p. 120–130° (lit.[1], 119–135°). (Found: C, 71.2; H, 7.4. $C_9H_{12}O_2$ calcd.: C, 71.6; H, 7.8%.) Mass spectrum gave the molecular ion at m/e 152, with the base peak at m/e 55 resulting from cleavage at the tertiary carbon and the bond α to the carbonyl. The bis(tosylhydrazone) (II) of this diketone was prepared from (I) by the method of Musso and Biethan[2]: m.p. 184–185° (decompn.) (lit., 200–201°). (Found: C, 57.0; H, 6.0; N, 11.1; S, 12.8. $C_{23}H_{28}N_4O_4S_2$ calcd.: C, 56.5; H, 5.8; N, 11.5; S, 13.1%.)

Bicyclo[3.3.1]nona-2,6-diene (III)
   Methyllithium[3] (0.36 mole) in ether (800 ml) was added dropwise over 45 min

to a suspension of the bis(tosylhydrazone) (II) (44 g, 0.09 mole) in ether (350 ml) stirred at room temperature under N_2. A vigorous reaction occurred with evolution of gas. The mixture was left stirring overnight, the excess methyllithium was then destroyed by addition of water. The layers were separated and the ether layer was washed, first with water then with sat. aq. NaCl and dried over Na_2SO_4. Distillation of the ether layer afforded a colourless liquid, b.p. 45–50°/5 mm, the IR and PMR spectra of which agreed with those published[2] for bicyclo[3.3.1]nona-2,6-diene (yield 60%). The mass spectrum gave the molecular ion at m/e 120 with the base peak at m/e 79 compatible with the structure of the diene (III).

Synthesis of diene–metal complexes

Complexes were prepared by normal literature methods (palladium, platinum: ref. 4, rhodium: ref. 5).

$C_9H_{12}PdCl_2$ *(IV)*. The diene (1.5 ml) was added to Na_2PdCl_4 (1.5 g) in methanol (50 ml) stirred under N_2 at room temperature. Yellow crystals appeared almost immediately. After 1 h these were filtered and recrystallised from acetic acid to yield orange, air stable crystals: m.p. 189–192° (decompn.). (Found: C, 36.4; H, 4.3; Cl, 23.8. $C_9H_{12}PdCl_2$ calcd.: C, 36.3; H, 4.0; Cl, 23.85%.)

$C_9H_{12}PtCl_2$ *(V)*. The diene (1.5 ml) was added to Na_2PtCl_4 (1.5 g) in isopropanol stirred at room temperature under N_2. After two days the mixture was filtered to yield air stable crystals which were recrystallised from a methylene chloride/hexane mixture. M.p. 203–206° (decompn.). (Found: C, 27.4; H, 3.1; Cl, 18.4. $C_9H_{12}Cl_2Pt$ calcd.: C, 27.8; H, 3.1; Cl, 18.8%.)

$(C_9H_{12}RhCl)_2$ *(VI)*. The diene (0.4 ml) and $RhCl_3 \cdot 3H_2O$ (0.4 g) were refluxed for 3 h under N_2 in 9 ml methanol/water (8/1), then left overnight. The mixture was filtered to yield orange, air stable crystals which were recrystallised from methylene chloride/petroleum ether (b.p. 40–60°). M.p. 203–205° (decompn.). (Found: C, 41.75; H, 4.8; Cl, 13.8. $C_{18}H_{24}Cl_2Rh_2$ calcd.: C, 41.8; H, 4.6; Cl, 13.7%.) The ready solubility and the mass spectrum are considered to be evidence against a polymeric structure.

The stability of the complexes towards hydrogen was determined by heating the solid complex in gaseous hydrogen in a static reaction system from which gas was allowed to bleed into a mass spectrometer.

RESULTS AND DISCUSSION

The structure of the diene and the structures attributed to the metal–diene complexes are shown in Fig. 1. With some qualifications the general characteristics of the complexes are similar to those of other diene–metal complexes.

PMR spectra (Table 1)

Although the spectrum of the diene has only one olefinic peak $(W_{\frac{1}{2}}$ 6 Hz) each complex displays two broad signals of equal intensity in the olefinic region. Such splitting has been found in the rhodium complex of cis,cis-1,5-cyclononadiene[6]; unfortunately measurement of the PMR of the corresponding Pd[II] and Pt[II] complexes was not possible because of insolubility. A complex of dicyclopentadiene also gives doubling of olefinic peaks[7]. The splitting of olefinic proton signals in the present complexes can be explained on either of two bases, and it is not possible at present to
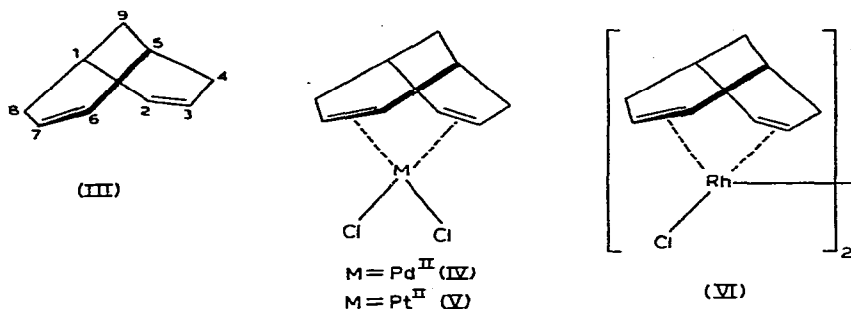
Fig. 1.

TABLE 1

PMR SPECTRA (60 MHz CCl$_4$) AND DECOMPOSITION TEMPERATURES

Compound	Chemical shifts (τ) of H			Decomp. Temp. in H$_2$ (°C)
	Olefinic	Methylene and bridgehead	Bridge	
Olefin	4.35	7.35–8.15	8.3	
(C$_9$H$_{12}$RhCl)$_2$	5.30, 6.11	6.70–8.10	8.80	150
C$_9$H$_{12}$PdCl$_2$	3.17, 4.12	6.35–7.95	8.20	20
C$_9$H$_{12}$PtCl$_2$	3.77, 4.70	6.55–7.75	8.30	190

distinguish between these. Firstly, in the bicyclononadiene complexes the two metal–olefin bonds may be equivalent, but the proton pairs H-2, H-6 and H-3, H-7 are not equivalent because the axis of each metal–olefin bond cannot lie in the plane of symmetry of the orbitals of the appropriate double bond. This is a consequence of the shape of the carbon framework in the ligand and its limited flexibility and leads to different shielding of the olefinic protons. Alternatively, the two metal–olefin bonds may be non-equivalent in that the metal atom location is such as to give a stronger bond to C-2 and C-3 (*vide infra*) but is then less well suited for bonding to C-6 and C-7. The non-equivalent proton pairs are then H-2, H-3 and H-6, H-7. The complex of the less symmetrical hydrocarbon dipentene with platinum(II) chloride provides a parallel for such a structure[8].

In the spectrum of C$_9$H$_{12}$PtCl$_2$ (V) coupling is observed between [195]Pt ($I=\frac{1}{2}$, 34% abundance) and the olefinic protons [J(Pt–H)=51 Hz]. In the rhodium complex (VI) ([103]Rh, $I=\frac{1}{2}$, 100% abundance) no analogous splitting is observed although the peaks are broad ($W_{\frac{1}{2}}$ 16 Hz). In the palladium complex where no metal–hydrogen coupling is possible the half-width of the olefinic proton signal is 15.5 Hz.

In the rhodium complex the olefinic proton signals are shifted upfield but the palladium complex shows a shift downfield, as to a lesser degree does the platinum complex. This behaviour is not peculiar to bicyclononadiene complexes; the norbornadiene complex of Rh[1] shows an olefinic shift upfield (from τ 3.38 to 6.12)[9] but the palladium complex shows a small shift downfield (from τ 3.38 to 3.22)[10]. For palladium complexes of *cis*- and *trans*-1,2 bis(dimethylarsino)ethylene a downfield

shift of 0.4–1.0 ppm is observed[11]. The difference in olefinic proton shift between the platinum and palladium complexes (IV) and (V) can be understood in terms of increased back-donation[12] in the former. Back-donation would be expected to be even greater in the rhodium complex (VI) both as a result of the greater ability of this metal to back-donate (for example, formation of carbonyls) and because bridging chlorine atoms are less electron withdrawing than bonded, but non-bridging chlorine atoms.

Mass spectra

As has been found[13] with other diene–palladium complexes no metal containing ions are observed in the mass spectrum of $C_9H_{12}PdCl_2$. With $C_9H_{12}PtCl_2$ several molecular ions are observed arising from isotopes of Pt (194,195,196) and Cl (35,37). Fragmentation occurs with loss of Cl, loss of Cl with some of the ligand to leave $ClPtC_6H_{10}^+$ and $ClPtC_6H_6^+$, loss of both Cl atoms and some of the ligand to leave $Pt–C_3H_4^+$ and $Pt–C_3H_3^+$. Most of the fragmentation results in wholly hydrocarbon ions giving a pattern which is very similar to that given by the diene itself. With $(C_9H_{12}RhCl)_2$ the molecular ions are observed at m/e 516–520. Fragmentation occurs with loss of HCl, loss of HCl and the diene, and with splitting of the dimer in half (m/e 258). Again most of the fragmentation results in wholly hydrocarbon ions, the pattern being very similar to that of the diene itself.

Decomposition in hydrogen (Table 1)

The extreme sensitivity of the palladium complex towards hydrogen may in part be attributed to the ease with which four co-ordinate palladium complexes expand their co-ordination number to six (necessary to activate hydrogen), the relative weakness of the palladium–olefin bond and its high susceptibility to nucleophilic attack[12]. The norbornadienepalladium(II) chloride complex is, however, stable to 160° in hydrogen which shows that the high reactivity is not inherent in the $>PdCl_2$ grouping. Maximum strength of bonding of a diene in a metal complex of the square-planar class will result when the plane of each double bond is perpendicular to the metal–olefin bond and to the plane determined by the metal and chlorine atom[14,15]. In norbornadiene complexes each of these conditions is fulfilled[15]. In bicyclononadiene complexes the planes of both double bonds cannot be at right angles either to the metal–olefin bond or to the plane of the complex. The metal–olefin bonds are in consequence weaker than in the norbornadiene complex. Further, if the first structure for the bicyclononadiene complexes discussed earlier proves to be the correct one, each olefinic bond is polarised (the appropriate interpretation of the NMR splitting of olefinic proton signals) and such bonds may be more susceptible to attack by hydrogen.

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