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Preliminary communication

Cycloheptatriene–rhodium(I) acetylacetonate

JOHN M. BROWN and DAVID G. COLES

Department of Molecular Sciences, University of Warwick, Coventry CV4 7AL (Great Britain)

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SUMMARY

Cycloheptatriene–rhodium(I) acetylacetonate has been prepared; the d_7 analogue undergoes deuterium scrambling at 60°.

In contrast to the range of h^6 (triene) and h^4 (conjugated diene) complexes of cycloheptatriene[1,2]* which have been proposed and characterised, very few examples of h^2,h^2 (non-conjugated chelating diene)[3]** complexes exist and in these the mode of bonding is inferred rather than defined.

The reaction of rhodium(I) complexes with cycloheptatriene has rather a chequere history, for Bonati and Wilkinson[5] reported that reaction of the olefin with dicarbonyl rhodium(I) acetylacetonate led to the isolation in low yield of bicyclo[2.2.1]heptadiene–rhodium(I) acetylacetonate. It was subsequently shown that this arises from traces of the isomeric olefin in commercial cycloheptatriene[6,7], and is not produced after careful prior purification. We find that the reaction of pure cycloheptatriene and diethylene rhodium(I) acetylacetonate in ether at 0° allowed the preparation of a crystalline complex*** (II) whose NMR spectrum is shown in Fig. 1 and which is clearly derived from unrearranged cycloheptatriene. Coupling constants are similar to those in the parent hydrocarbon and in particular the values $J_{1,7exo}$ 4 Hz and $J_{1,7endo}$ 7.5 Hz are in keeping with minimal distortion of geometry. The chemical shifts of H_2 (upfield) and H_1 (downfield) are the reverse of observations on h^6-complexes, or the parent hydrocarbon[8]. Although stable to 90° in hydrocarbon solvents, (II) is degraded over the course of a few hours in carbon

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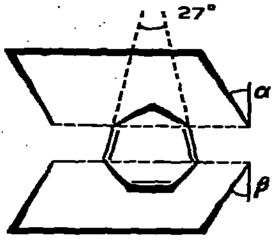
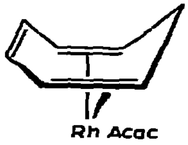
* Copper and silver complexes of indeterminate hapticity have been prepared[2].

** Although cycloheptatriene is similar to cyclooctatetraene in ring puckering ($\alpha = 40.5°$; $\beta = 36°$, in (I))[4] a major hindrance to chelation may be the inability of the 1,2 and 4,5 double bonds to align in parallel planes.

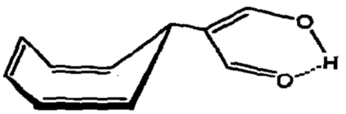
*** Satisfactory combustion analysis.



(I)



(II)



(III)

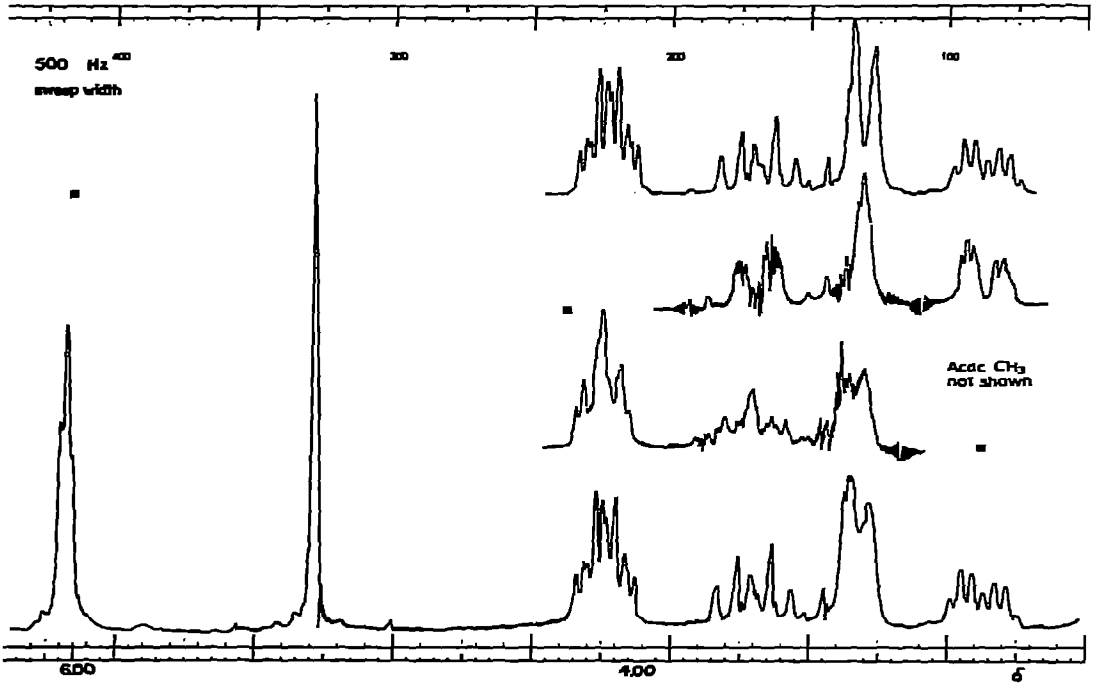


Fig.1. PMR spectrum of (II) in C_6D_6 with δ 6.03 (H_3, $J_{2,3} < 2$ Hz) 5.14 (AcacC–H) 4.09 (H_1, $J_{1,2}$ 10 Hz, $J_{1,7\text{-}exo}$ 4 Hz, $J_{1,7\text{-}endo}$ 7.5 Hz) 3.56 ($H_{7\text{-}endo}$, $J(\text{Rh})_{7\text{-}endo} < 1$ Hz) 3.18 (Hz) 2.74 ($H_{7\text{-}exo}$, $J(^{103}\text{Rh})_{7\text{-}exo}$ 4 Hz) 1.75 (AcacCH_3) ppm.

tetrachloride and acetylacetonylcycloheptatriene (III)[9] (identified by NMR; m.p. and mixed m.p. 124°) could be isolated in low yield.

Since sigmatropic hydrogen shifts occur more rapidly in Group VII complexes than in the parent hydrocarbon[10,11] and specific *endo*-migration[*] is involved, we explored the possibility of a similar reaction in (II). Rapid isomerisation is precluded by the lack of change in the NMR spectrum up to 85°, and we therefore prepared the analogue

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[*] *endo*-Hydrogen-migration occurs in 7-*exo*-[^{2}H]-cycloheptatrieneiron tricarbonyl[11a] at 75° [11b].

derived from 7-[^{2}H]-cycloheptatriene (from tropylium tetrafluoroborate and $LiAlD_4$). At 60° (Table 1) isomerisation occurs, and recovery of cycloheptatriene by NaCN treatment after 18 h shows extensive scrambling. In the initial phases of reaction, 7-*exo*-protium appeared to grow faster than 7-*endo*-protium, in keeping with selective *endo*-migration. Recovered cycloheptatriene had much less than 0.5 atom of deuterium at the 7-position, from which we infer that exchange with a trace of free cycloheptatriene masks the overall selectivity of scrambling at long reaction times[12].

TABLE 1

DEUTERIUM DISTRIBUTION IN (II) ESTIMATED FROM THE 60 MHz NMR SPECTRUM BY DUPLICATE TRACINGS AND WEIGHINGS (The non-random distribution appears real, but the accuracy of the experiment precludes a more detailed analysis.)

	Number of hydrogen atoms at			
	$C_{1,6}$	$C_{2,5}$ + C_7-*endo*	$C_{3,4}$	C_7-*exo*
Initial	2.00	2.45	1.90	0.60
60°/30 min	1.85	2.55	1.95	0.70
60°/90 min	1.90	2.50		0.85
60°/1080 min	1.70	2.50	1.80	1.00
Recovered cycloheptatriene	1.80	1.50	1.70	2.00[a]

[a] *exo* and *endo*

A more sensitive probe than migration of 0.5 atom deuterium is required to define the course of hydrogen migration, and we hope to carry out experiments with 7-^{13}C-cycloheptatriene in the future.

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