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INTRAMOLECULAR REARRANGEMENT IN DIPHENYLFULVENE COMPLEXES OF IRIDIUM(I) AND RHODIUM(I)

E.J. PROBITTS and R.J. MAWBY
Department of Chemistry, University of York, York YO1 5DD (Great Britain)

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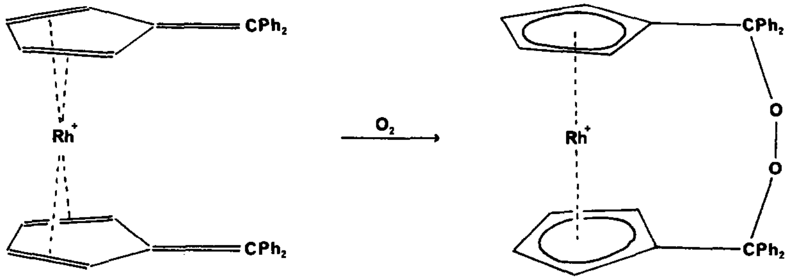
Summary

Variable temperature NMR spectra of the complexes $[M(C_5H_4CPh_2)(C_8H_{12})]X$ ($C_5H_4CPh_2$ = 6,6-diphenylfulvene; C_8H_{12} = 1,5-cyclooctadiene; M = Ir, X = PF_6; M = Rh, X = ClO_4) provide evidence of intramolecular rearrangement involving rotation of the diphenylfulvene ligand about the metal–fulvene axis. Rearrangement is slow on the NMR time-scale for both complexes at 223 K: spectra recorded at higher temperatures indicate that the barrier to rotation of the diphenylfulvene ligand is lower for the iridium than for the rhodium complex.

Introduction

Recently we have reported an unusual reaction of bis(6,6-diarylfulvene) complexes of rhodium(I) with dioxygen, which results in the insertion of the dioxygen molecule as a peroxide bridge between the exocyclic carbon atoms of the two organic ligands, giving what are, in effect, bis(cyclopentadienyl) complexes of rhodium(III) [1,2]. The reaction of the bis(diphenylfulvene) complex is shown.



A crystallographic study of a "model" complex of rhodium(I) containing a single fulvene ligand, $[Rh(C_5H_4CPh_2)(C_8H_{12})]ClO_4$ ($C_5H_4CPh_2$ = 6,6-diphenylfulvene,

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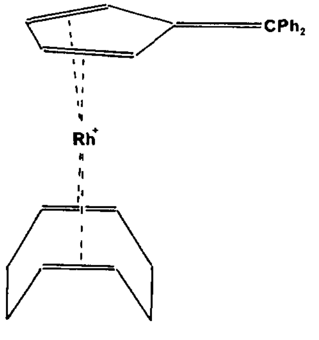
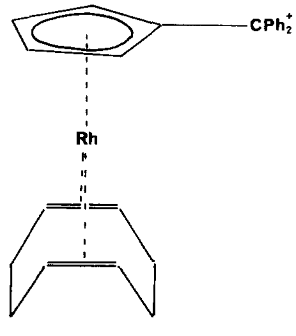
C_8H_{12} = 1,5-cyclooctadiene) revealed a mode of metal–fulvene bonding best described as a hybrid of the two resonance structures **A** and **B** [3].



(A)



(B)

This raises an interesting point. The presence of the fulvene ligand lowers the symmetry of the 1,5-cyclooctadiene ligand, leading one to expect two resonances for its CH carbon atoms (and for their attached hydrogen atoms), two for the CH_2 carbon atoms and four for their attached hydrogen atoms in the ^{13}C and ^1H NMR spectra of the complex. In solution, however, rapid rotation of the fulvene ligand about the metal–fulvene bond might occur, simplifying the spectra. Such rotation might reasonably be expected in the case of the cyclopentadienyl-like structure **B**, but not for **A**: this essentially planar four-coordinate complex of rhodium(I) would become tetrahedral in the course of the rotation of the fulvene ligand.

In our earlier paper [2] we noted that the ^1H and ^{13}C NMR spectra of $[Rh(C_5H_4CPh_2)(C_8H_{12})]ClO_4$ altered in appearance with temperature. Here we present a fuller report of the temperature dependence of the NMR spectra of this complex, and of an analogous iridium(I) complex, $[Ir(C_5H_4CPh_2)(C_8H_{12})]PF_6$.

Results and discussion

Details of the limiting low-temperature ^1H and ^{13}C NMR spectra of CD_3COCD_3 solutions of the complexes are given in Tables 1 and 2 respectively. At 223 K, the ^1H NMR spectrum of $[Ir(C_5H_4CPh_2)(C_8H_{12})]PF_6$ exhibited the two resonances expected for the inequivalent pairs of CH protons in the 1,5-cyclooctadiene ligand at δ 4.99 and 5.85. Of the four expected CH_2 proton resonances for the diene ligand, two were virtually superimposed at δ 2.51, the other two being at δ 2.29 and 2.87. As the temperature was raised, the two CH proton resonances broadened, coalesced and resharpened, giving a single fairly sharp resonance at δ 5.54 in a spectrum recorded at 321 K. Over the same temperature range, one of the two CH_2 resonances at δ 2.51 coalesced with that at δ 2.29, the other with that at δ 2.87, giving resonances at δ 2.42 and 2.70 in the spectrum recorded at 321 K. Similarly the two CH carbon atom resonances for the diene ligand (at δ 75.7 and 76.8) coalesced to a single peak at δ 77.0, and those for the CH_2 carbon atoms (at δ 32.6 and 35.4) gave a single peak at δ 34.7. Apart from minor changes in chemical shift, the ^1H and ^{13}C resonances due to the fulvene ligand did not alter in appearance between 223 and 321 K. All the changes in the resonances for the diene ligand were reversed when the solution was returned to 223 K.

TABLE 1

^{1}H NMR SPECTRA[a]

$[Ir(C_5H_4CPh_2)(C_8H_{12})]PF_6$	$[Rh(C_5H_4CPh_2)(C_8H_{12})]ClO_4$	Assignment
2.29(2)	2.35(2)	diene, CH_2
2.51(4)[b]	2.54(4)[b]	diene, CH_2
2.87(2)	[c]	diene, CH_2
4.99(2)	5.36(2)	diene, CH
5.81(2)	5.80(2)	fulvene
5.85(2)	5.85(2)	diene, CH
7.06(2)	6.96(2)	fulvene

[a] Spectra were recorded on CD_3COCD_3 solutions at 223 K (Ir complex) and 233 K (Rh complex). Chemical shifts are given on the δ scale (ppm) and are followed by relative areas of resonances, all of which were multiplets. For the fulvene ligand, only the resonances for the protons in the five-membered ring are listed. [b] Two superimposed resonances. [c] Obscured by resonance due to incompletely deuterated CD_3COCD_3.

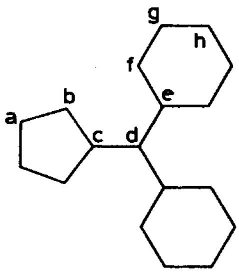
Similar changes were noted in the ^{1}H and ^{13}C NMR spectra of $[Rh(C_5H_4CPh_2)(C_8H_{12})]ClO_4$ with increasing temperature, although the information obtained was less complete because the averaged resonances were still broad at 323 K (above

TABLE 2

^{13}C NMR SPECTRA[a]

$[Ir(C_5H_4CPh_2)(C_8H_{12})]PF_6$	$[Rh(C_5H_4CPh_2)(C_8H_{12})]ClO_4$	Assignment
32.6(s)	[b]	diene, CH_2
35.4(s)	[b]	diene, CH_2
75.7(s)	90.5(d, 10 Hz)	diene, CH
76.8(s)	93.1(d, 11 Hz)	diene, CH
82.3(s)	86.9(d, 5 Hz)	fulvene, a or b
104.8(s)	106.7(d, 5 Hz)	fulvene, a or b
114.8(s)	119.4(d, 4 Hz)	fulvene, c
129.4(s)	129.9(s)	fulvene, f or g
130.2(s)	131.9(s)	fulvene, f or g
131.2(s)	132.1(s)	fulvene, h
141.0(s)	156.3(s)	fulvene, d
142.0(s)	141.1(s)	fulvene, e

[a] Spectra were recorded on CD_3COCD_3 solutions at 223 K. Chemical shifts are given on the δ scale (ppm), and are followed by multiplicities and, where appropriate, values of $|J(Rh-C)|$. The lettering system for the fulvene resonances is as follows:



[b] Obscured by resonance due to solvent.

which temperature the complex decomposed at a significant rate), and because of masking of some of the CH_2 resonances by solvent resonances. At 323 K the averaged CH proton and carbon resonances were at δ 5.50 and 93.4 respectively, and one of the averaged CH_2 proton resonances was visible at δ 2.48 (the other being obscured by resonances due to incompletely deuterated CD_3COCD_3). The CH_2 carbon resonances were largely hidden by the resonance due to the CD_3 carbon atoms in the solvent. Again the resonances due to the fulvene ligand were unchanged over the full temperature range studied (apart from minor alterations in chemical shift), and the changes in appearance of the resonances for the diene ligand were reversed on cooling.

Two key features of the spectra should be noted. Firstly, the ^1H NMR spectrum of $[Ir(C_5H_4CPh_2)(C_8H_{12})]PF_6$ still exhibited two CH_2 proton resonances even at the highest temperature studied. A rearrangement process involving dissociation and reassociation of the diene ligand would have resulted in all eight CH_2 protons becoming equivalent. Secondly, the doublet splittings (see Table 2) observed for the carbon atoms in the five-membered ring of the fulvene ligand in $[Rh(C_5H_4CPh_2)(C_8H_{12})]ClO_4$, and attributed to coupling to the ^{103}Rh nucleus, persisted over the entire temperature range, ruling out dissociation and reassociation of the fulvene ligand. Thus the rearrangement responsible for the simplification of the NMR spectra at higher temperatures was an intramolecular process, presumably involving rotation of the fulvene ligand about the metal–fulvene axis.

Comparison of the spectra of the two complexes indicated that at a given temperature, rotation of the fulvene ligand was significantly faster for the iridium complex than for the rhodium complex. From the crystal structure of $[Rh(C_5H_4CPh_2)(C_8H_{12})]ClO_4$ [3], there appears to be no reason to expect a significant steric barrier to rotation, so this could be an indication that the balance between resonance structures of types **A** and **B** is shifted further in favour of **B** for iridium than it is for rhodium.

Finally, it is noteworthy that rotation of the fulvene ligand about the metal–fulvene axis has also been proposed as an explanation for the temperature dependence of the ^{13}C NMR spectrum of the chromium(0) fulvene complex $[Cr(CO)_3(C_5H_4CH_2)]$. At low temperatures two resonances are observed for the carbonyl ligands, whereas at higher temperatures all three appear to become equivalent. Here, however, the fulvene is acting as an η^6-bonded triene ligand [4].

Experimental

The preparation of $[Rh(C_5H_4CPh_2)(C_8H_{12})]ClO_4$ has been described in an earlier paper [2].

Preparation of $[Ir(C_5H_4CPh_2)(C_8H_{12})]PF_6$

This was prepared from $[Ir_2Cl_2(C_8H_{12})_2]$ [5], using a technique similar to that described by Schrock and Osborn for the preparation of arene and diene complexes of iridium(I) [6]. All operations were carried out under N_2. A solution of $[Ir_2Cl_2(C_8H_{12})_2]$ (0.146 g) in tetrahydrofuran (30 cm^3, freshly distilled under N_2 from sodium and benzophenone) was stirred in the absence of light with $AgPF_6$ (0.110 g). After 20 min the solution was filtered and the filtrate treated with a solution of 6,6-diphenylfulvene (0.103 g) in tetrahydrofuran (10 cm^3). The solution, which immediately turned purple, was cooled in ice for 9 h. Purple needles were formed. The mother liquor was removed, and the crystals were washed with a small volume of cold tetrahydrofuran and dried in vacuo (Found: C, 46.40; H, 4.08. $C_{26}H_{26}F_6IrP$ calcd.: C, 46.22; H, 3.88%.) Warning: the related compound $[Ir(C_5H_4CPh_2)(C_8H_{12})]ClO_4$, obtained using $AgClO_4$ in place of $AgPF_6$, decomposed vigorously on scraping.

Spectroscopic studies

The ^1H and ^{13}C NMR spectra were recorded on CD_3COCD_3 solutions of the complex, using a JEOL FX-90Q spectrometer, with operating frequencies for ^1H and ^{13}C of 90.0 and 22.5 MHz respectively. The spectrometer was fitted with a JEOL NM-5471 variable temperature attachment.

Acknowledgements

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References

1 J. Jeffery, R.J. Mawby, M.B. Hursthouse and N.P.C. Walker, J. Chem. Soc., Chem. Commun., (1982) 1411.
2 J. Jeffery, E.J. Probitts and R.J. Mawby, J. Chem. Soc., Dalton Trans., (1984) 2423.
3 Z. Dauter, L.K. Hansen, R.J. Mawby, E.J. Probitts and C.D. Reynolds, Acta Crystallogr., C, 41 (1985) 850.
4 O. Koch, F. Edelmann and U. Behrens, Chem. Ber., 115 (1982) 1313.
5 R.H. Crabtree and G.E. Morris, J. Organomet. Chem., 135 (1977) 395.
6 R.R. Schrock and J.A. Osborn, J. Am. Chem. Soc., 93 (1971) 3089.