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DIENE AND DIENYL COMPLEXES OF TRANSITION ELEMENTS

VI *. THE PROTONATION OF TWO ISOMERIC (η^5-CYCLOPENTADIENYL)(η^4-1,7-DIPHENYLHEPTATRIEN-1-ONE)RHODIUM(I) COMPLEXES

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Summary

Two isomeric complexes [Rh{2-5-η-PhCO(CH)$_4$CH=CHPh}(η^5-C_5H_5)] and [Rh{4-7-η-PhCOCH=CH(CH)$_4$Ph}(η^5-C_5H_5)] have been prepared. The former reacts with HBF_4 to give the salt [Rh{η^3-PhCOCH$_2$(CH)$_3$CH=CHPh}(η^5-C_5H_5)]$^+$ BF_4^- in which the acyl CO group is coordinated to the metal. The latter, however, on treatment with HPF_6, yields a η^5-pentadienyl salt [Rh{η^5-PhCOCH$_2$(CH)$_5$Ph}(η^5-C_5H_5)]$^+$ PF_6^-. ^{1}H and some ^{13}C NMR spectra are reported.

Introduction

The standard method of preparation of η^5-pentadienyltricarbonyliron salts is by protonation of η^4-dienoltricarbonyliron complexes [2,3]. We have shown that this method can also be applied to the synthesis of (η^5-cyclopentadienyl)(η^5-pentadienyl)rhodium and iridium cations [4]. Another approach is through protonation of η^4-hexatriene complexes. In the iron series this has been used both for cyclic [5] and open chain [6] trienes. Similarly, η^4-cyclooctatriene-η^5-cyclopentadienylrhodium, [Rh(η^4-C_8H_{10})(η^5-C_5H_5)] affords cations [Rh(η^5-C_8H_{11})(η^5-C_5H_5)]$^+$ in which the C_8H_{11} entity adopts a variety of bonding modes [7]. To our knowledge, however, the method has not been applied to the synthesis of open chain η^5-pentadienyl salts of rhodium.

Several years ago Whitlock prepared isomeric tricarbonyliron complexes of unsymmetrically substituted 1,6-diaryl-1,3,5-trienes, [Fe(CO)$_3${η^4-Ph(CH)$_4$CH=CHAr] and [Fe(CO)$_3${η^4-PhCH=CH(CH)$_4$Ar}] [8,9]. He found that these isomers are stable to rearrangement at room temperature and that they interconvert only

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* For part V see ref. 1.

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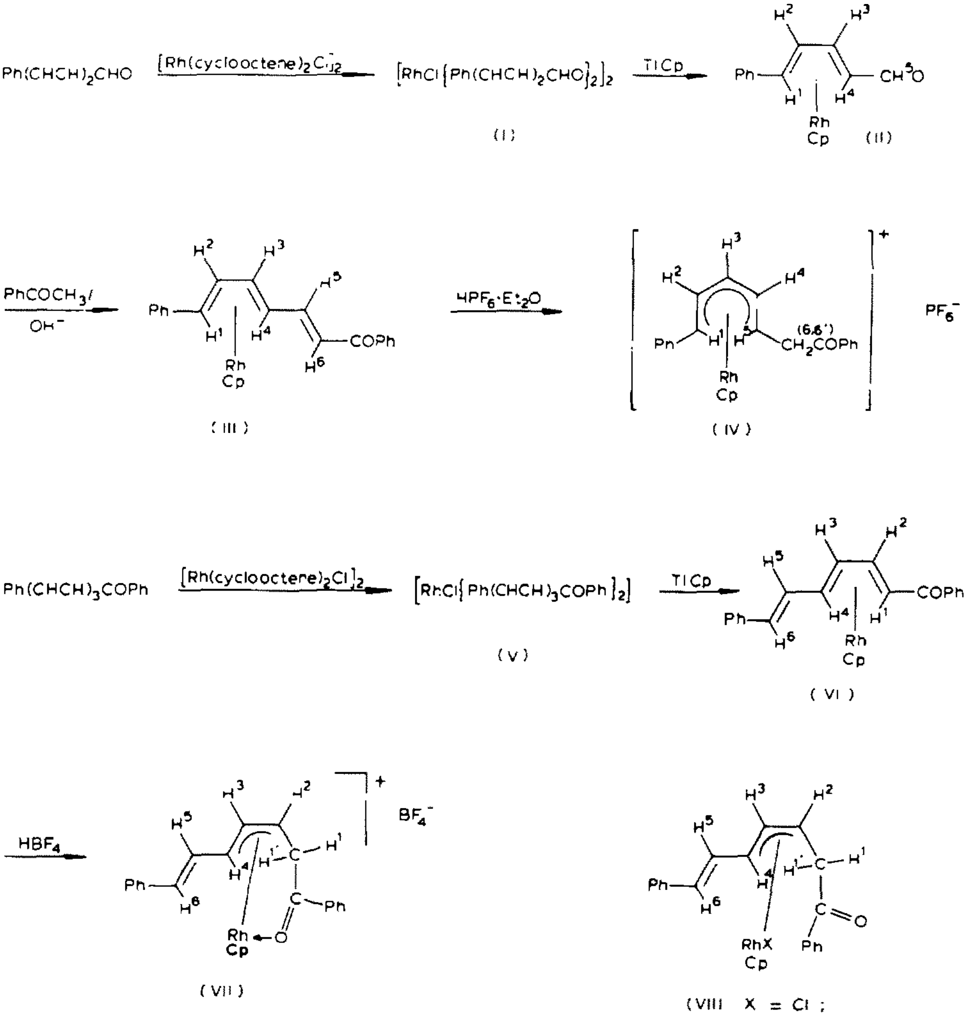
slowly at 99.6°C. It was of interest to investigate whether similar isomeric η^5-cyclopentadienylrhodium complexes could also be isolated without undergoing rearrangement. This paper describes the preparation of two isomeric η^5-cyclopentadienylrhodium complexes of 1,7-diphenylheptatrien-1-one and their differing behaviour on protonation.

Results and discussion

The preparation of the isomeric complexes is shown in Scheme 1. Reaction of 5-phenyl-2,4-pentadien-1-al [10] with bis(cyclooctene)chlororhodium in diethyl ether yields the 1 : 1 complex I. Treatment of I with thallium cyclopentadienide in dichloromethane affords (η^4-5-phenyl-2,4-pentadienal)(η^5-cyclopentadienyl)rhodium (II), which undergoes base catalysed condensation with acetophenone to give III. The ^{1}H NMR spectrum of III is consistent with η-4-7 bonding of the 1,7-diphenyl-



SCHEME 1

2,4,6-heptatrienone ligand to rhodium. Reaction of III with hexafluorophosphoric acid diethyl etherate in diethyl ether affords the substituted η^5-pentadienyl salt, IV. The ^{1}H NMR spectrum of IV was measured both in CD_2Cl_2 and also in CD_3NO_2 (see Table 1). As for other η^5-pentadienyl salts [2,3,4] the proton H(3) attached to the central carbon atom of the η^5-system (6.72δ, triplet) resonates to low field of the protons on adjacent carbon atoms, H(2) (6.34δ, doublet of doublets) and H(4) (5.83δ, doublet of doublets). A doublet at 4.20δ is assigned to H(1). These assignments were confirmed by irradiation at 5.83δ, when the triplet at 6.72δ collapsed to a doublet, and a multiplet at 3.61δ(H(5)) to a broad triplet. The resonance at 4.20δ(H(1)) was unaffected, although that at 6.34δ(H(4)) now revealed a further small coupling of 1.2 Hz, probably to the ^{103}Rh nucleus.

In the ^{13}C NMR spectra of $[Rh(\eta^5\text{-}C_5H_5)(\eta^5\text{-}MeC_5H_6)]^+$ and of $[M(\eta^5\text{-}C_5H_5)\text{-}\{\eta^5\text{-}Ph(CH)_5Ph\}]^+$ (M = Rh, Ir), the resonance of the central carbon nucleus of the pentadienyl system, C(3), lies to low field of those of C(2) and C(4) [4,11]. This contrasts with observations on tricarbonylpentadienyliron salts [12,13] and on tricarbonylpentadienylmanganese [14] in which the resonances of C(2) and C(4) lie to low field of that of C(3). If ^{13}C NMR shifts can be taken to parallel electron density at carbon centres within a molecule, and even within a series of closely related molecules [15], these results suggest that in the rhodium and iridium cations C(3) bears the greatest positive charge. This is consistent with the observation that cyclopentadienyl(-1-methylpentadienyl-rhodium and -iridium add nucleophiles at C(3) [16], although it must be remembered that there is not a correlation between charge density and the site of nucleophilic attack in the tricarbonyliron series [17]. The ^{13}C NMR spectrum of IV was assigned on the basis of selective irradiation at specific proton frequencies. In contrast with the pattern of shifts discussed above, C(4) (97.4 ppm) resonates a little to low field of C(3) (96.5 ppm) and C(2) (92.3 ppm). The ^{103}Rh–^{13}C coupling constants are greater to the terminal carbon atoms C(1) and C(5) (10.2 Hz), than to the inner carbon atoms C(2), C(3) and C(4) (all 6.1 Hz) of the pentadienyl system, in agreement with observations on similar compounds [18].

The isomer of III, (2-5-η-1,7-diphenyl-2,4,6-heptatrien-1-one)(η^5-cyclopentadienyl)rhodium(VI) was prepared starting from 1,7-diphenyl-2,4,6-heptatrien-1-one itself. Reaction of the trienone with bis(cyclooctene)chlororhodium in diethyl ether gives V, which was shown by elemental analysis to be the 2 : 1 complex. The ^{1}H NMR spectrum of V in $CDCl_3$, however, indicated that dissociation of one trienone ligand occurs in solution. The triene, however is bonded to the metal exclusively through the four carbon atoms adjacent to the carbonyl group. This mode of bonding is presumably preferred as it results in the electron attracting -COPh group being adjacent to the η^4-bonded system. This leads to better back bonding from the electron rich metal centre to the trienone ligand than in the other isomeric arrangement in which the -COPh group is more remote. Treatment of V with thallium cyclopentadienide afforded VI, although TLC of the crude reaction mixture indicated that a trace of III was also present. Compound VI has a benzoyl substituent on C(1), and on protonation with tetrafluoroboric acid it yields the η^3-complex VII. This behaviour is analogous to that of (η^4-1,5-diphenyl-2,4-pentadienone)(η-cyclopentadienyl)rhodium [19]. In the infrared spectrum of VII, there are two peaks at 1584 and 1566 cm^{-1}. The second of these is broader and somewhat more intense and is assigned to ν(CO), the other probably being due to aromatic or C=C

TABLE 1

^{1}H NMR DATA FOR THE COMPLEXES[a]

Complex	Chemical shifts (δ, ppm)				
	H(1)	H(1′)	H(2)	H(3)	H(4)
II	2.81(d) J(H(2))7.3		5.55(m)	5.46(m)	1.91(t) J(H(3), H(5))6.9
III	2.64(dd) J(H(2))8.0 J(Rh)1.8		5.39(m) J(H(1))8.0 J(H(3))4.5 J(Rh)1.8	5.29(m) J(H(5))7.0 J(H(3))4.5 J(Rh)1.5	2.33(t)
IV[c]	4.20(d) J(H(2))11.3		6.34(dd) J(H(1))11.3 J(H(3))7 J(Rh)1.2	6.72(t) J(H(2), H(4))7	5.83(dd) J(H(3))7 J(H(5))10.5
V	3.42(d) J(H(2))9.5		6.70(dd) J(H(1))9.5 J(H(3))5.3	4.70(dd) J(H(2))5.3 J(H(4))11.3	4.38(t) J(H(4)), H(5))10.9
VI	2.60(dd) J(H(2))7.7 J(Rh)1.8		5.90(m) J(H(1), H(3))	5.30(m) J(H(2))4.5 J(H(4))7.5	2.79(t)
VII	4.19(dd) J(H(1′))21.2 J(H(2))8.0	3.43(dd) J(H(1))21.2 J(H(2))2.0	6.02(td)	5.73(ddd)	4.02(dd) J(H(3))11.7 J(H(5))8.8
VIII	2.89(dd) J(H(1′))19.0 J(H(2))8.8	3.49(dd) J(H(1))19.0 J(H(2))5.5	5.29(m)	5.21(m)	4.72(t) J(H(5))10.2
IX	3.04(dd) J(H(1′))18.6 J(H(2)9.1	3.61(dd) J(H(1))18.6 J(H(2))4.7	5.31(m)	5.09(t)	4.89(t) J(H(5))10.2 J(H(3))11.4

[a] For numbering see Scheme 1. Measured at 250 MHz relative to tetramethylsilane, δ 0 ppm. Coupling constants in Hz. In $CDCl_3$ except for compounds IV (CD_2Cl_2) and VII (CD_2Cl_2). [b] Obscured by Ph resonances. [c] ^{13}C NMR spectrum in CD_3NO_2 ppm from TMS: 198.4 (CO), 140.2, 137.6, 135.2, 130.8,

vibrations. As suggested previously the low ν(CO) frequency in the spectrum of VII compared with 1642 cm^{-1} in that of its precursor VI is consistent with coordination of the acyl oxygen to rhodium, so that the 18-electron configuration of the metal atom is preserved. Assignment of the ^{1}H NMR spectrum of VII follows from our previous work.

The trienone complex VI yields deep maroon air stable derivatives VIII and IX with hydrogen chloride and hydrogen bromide respectively. The infrared spectra of VIII and IX show strong ν(CO) bands at 1684 and 1677 cm^{-1} respectively. Coordination of the acyl carbonyl group therefore does not occur here. This behaviour is entirely analogous to that of the η^4-dienone complexes discussed elsewhere. The ^{1}H NMR spectra (Table 1) are assigned accordingly, aided by some double resonance experiments.

H(5)	H(6)	H(6′)	C_5H_5	Ph resonances
9.05(d) J(H(4))6.9			4.99(d) J(Rh)1.1	7.26(s), 7.23(d) 7.15(m)
7.1(m)	7.1(m)		4.91(d) J(Rh)1.1	7.95(m), 7.47(m) 7.23(m)
3.61(m)	3.93(dd) J(H(6′))18.3 J(H(5))6.3	3.73(dd) J(H(6))18.3 J(H(5))6.0	5.49(d) J(Rh)1.1	8.05(m), 7.4–7.7(m)
6.04(dd) J(H(4))10.3 J(H(6))15.4	^{b}			8.00(m), 7.04(m), 6.87(m) 7.34(m), 7.26(m)
6.26(dd) J(H(4))10.0 J(H(6))15.7	6.64(d) J(H(5))15.7		4.99 J(Rh)1.5	8.1(m), 7.5(m) 7.3(m)
7.0(m)	7.0(m)		5.62(d) J(Rh)1.7	7.89(m), 7.75(m), 7.5(m) 7.35(m)
6.64(dd) J(H(6))15.7 J(H(4))10.2	7.04(d) J(H(5))15.7		5.35 J(Rh)1.1	7.95(m), 7.5(m), 7.4(m) 7.26(m)
6.61(dd) J(H(6))15.7 J(H(4))10.2	7.03(d) J(H(5))15.7		5.39(d) J(Rh)1.1	7.92(m), 7.5(m) 7.42(m), 7.26(m)

130.5, 130.3, 129.5, 128.3 (Ph); J(Rh–C), J(C–H): 97.4, 6.1 Hz, 169 Hz (C(4)); 96.5, 6.1 Hz, 169 Hz (C(3)); 93.5, 6.1 Hz, 185 Hz (C_5H_5); 92.3, 6.1 Hz, 169 Hz (C(2)); 83.4, 10.2 Hz, 166 Hz (C(1)); 79.6, 10.2 Hz, 170 Hz (C(5)); 46.4, –, 129 Hz (C(6)).

Experimental

Reactions were carried out under dry nitrogen, although most of the complexes are essentially stable to air both in the solid state and in solution. Microanalyses were by Butterworth Laboratories Ltd. Infrared spectra were determined as Nujol mulls on a Perkin–Elmer 257 spectrometer and were calibrated with polystyrene film. ^1H and ^{13}C NMR spectra were recorded using a Bruker 250 MHz instrument at King's College, University of London.

5-Phenyl-2,4-pentadien-1-al (m.p. 43°C) was obtained by the method of Marshall and Whiting [10]. 1,7-Diphenyl-2,4,6-heptadien-1-one was prepared by the base catalysed condensation of this aldehyde with acetophenone in 95% ethanol. After recrystallisation from ethanol it had m.p. 82–83°C.

Preparation of compounds I, II, V and VI

The general methods described earlier were followed [11]. Characterising data are given in Table 2.

Protonation of (4-7-η-1,7-diphenyl-2,4,6-heptadien-1-one)(η^5-cyclopentadienyl)rhodium

The ketone complex, III (0.114 g) was dissolved in dry diethyl ether (30 cm^3) and cooled to −70°C. Hexafluorophosphoric acid diethyl etherate (0.1 cm^3) was added and the mixture allowed to warm up slowly to room temperature with stirring. The brown precipitate was filtered off and crystallised first by dissolving in nitromethane and addition of ether and then likewise from dichloromethane/ether. The product IV was obtained as a yellow powder (0.125 g, 84%).

Base catalysed condensation of II with acetophenone

(η^4-5-Phenyl-2,4-pentadien-1-al)(η^5-cyclopentadienyl)rhodium (II) (0.326 g) and acetophenone (0.12 g) in ethanol (3 cm^3) was warmed to 50°C for 2 h with potassium hydroxide (50 mg) in water (0.3 cm^3). The colour of the solution changed from orange to maroon. Water (20 cm^3) was then added and the reaction mixture extracted with diethyl ether. The ether extracts were washed with water and dried over anhydrous calcium chloride. Ether was removed to leave a maroon oil which was chromatographed on silica gel. Ether/cyclohexane (1/10 v/v) eluted a yellow band (free trienone). The product (III) was eluted as a deep red band with ether/cyclohexane (1/2 v/v). Yield 0.114 g (38%). Unchanged II (0.12 g) (33%) was recovered with ether.

Protonation of VI

(2-5-η-1,7-Diphenyl-2,4,6-heptatrien-1-one)(η^5-cyclopentadienyl)rhodium, VI, (25

TABLE 2

ANALYTICAL AND SPECTROSCOPIC DATA FOR THE COMPLEXES

Complex	Colour	Yield (%)	M.p. (°C)	Analysis (%) [a]		IR (cm^{-1}) [b]
				C	H	
I	Red-brown	96	138–139 (decomp.)	47.4 (44.6)	4.1 (3.4)	1689
II	Orange	70	126	58.9 (58.9)	4.7 (4.6)	1672
III	Red	38	141	67.3 (67.3)	5.2 (4.9)	1652, 1602, 1584, 1574
IV	Orange	84	150 (decomp.)	49.2 (49.3)	3.8 (3.6)	1686
V	Red-brown	94	155–157 (decomp.)	69.0 (69.2)	5.0 (4.9)	1642
VI	Red	48	106	67.3 (67.3)	4.9 (4.9)	1642, 1596, 1578
VII	Orange	80	155 (decomp.)	49.5 (49.3)	3.8 (3.6)	1594, 1566
VIII	Maroon	75	103–104	62.0 (60.8)	4.8 (4.8)	1684
IX	Maroon	48	110–112	56.7 (56.6)	4.4 (4.4)	1677

[a] Calculated values are given in parentheses. [b] Nujol mull; ν(CO).

mg) was dissolved in $CDCl_3$ in an NMR tube, cooled to −78°C, and trifluoroacetic acid (0.05 cm^3) added. The tube and contents were allowed to warm up to ambient temperature and the NMR spectrum was recorded. After 0.5 h the mixture was poured into diethyl ether (50 cm^3) which contained tetrafluoroboric acid (0.4 cm^3, 40% aqueous). The resulting orange precipitate was filtered off, dissolved in nitromethane, filtered and reprecipitated with ether. Yield 24 mg (80%).

Reaction of VI with hydrogen chloride

Complex VI (0.135 g) in diethyl ether (20 cm^3) was treated with concentrated aqueous hydrochloric acid (0.05 cm^3) and the mixture stirred for 1 h. The pink precipitate was filtered off, dissolved in dichloromethane and filtered. On addition of petroleum ether (50 cm^3) b.p. 40–60°C and cooling to 0°C overnight, the product VIII (0.110 g, 75%) was obtained as red crystals.

Complex IX was obtained similarly using concentrated aqueous hydrobromic acid.

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