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DIENE AND DIENYL COMPLEXES OF TRANSITION ELEMENTS

V *. PREPARATION OF η-CYCLOPENTADIENYL-η-METHYL DIENOATE-RHODIUM AND -IRIDIUM COMPLEXES: BASE HYDROLYSIS AND PROTONATION STUDIES

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Summary

Reaction of [M(η^4-RCH=CHCH=CHCOOMe)(η^5-C_5H_5)] (M = Rh or Ir; R = Me or Ph) with HPF_6 affords crystalline salts [M(η^3-RCHCHCHCH$_2$COOMe)(η^5-C_5H_5)]$^+$ PF_6^- in which the acyl CO group is coordinated to the metal. Base-catalysed hydrolysis of the η^4-ester complexes affords the dienoic acid derivatives [M(η^4-RCH=CHCH=CHCOOH)(η^5-C_5H_5)]. The protonation of the 3,5-heptadien-1-one complexes [M(η^4-CH_3CH=CHCH=CHCOCH$_3$)(η^5-C_5H_5)] with HPF_6 proceeds similarly. The ^1H NMR spectra of the compounds are reported.

Protonation of (η^4-diaryldienone)(η^5-cyclopentadienyl)-rhodium and -iridium complexes [M(η^4-PhCH=CHCH=CHCOPh)(η^5-C_5H_5)] with acids HY having weakly coordinating anions (Y = CF_3COO, BF_4 or PF_6) yields η^3-allylic complexes [M(η^3-PhCHCHCHCH$_2$COPh)(η^5-C_5H_5)]Y in which the acyl carbonyl group is coordinated to the metal [2]. In order to test how general this behaviour is, we have investigated the protonation of the complexes [M(η^4-RCH=CHCH=CHCOQ)(η^5-C_5H_5)] (M = Rh or Ir, Q = OMe or Me) with hexafluorophosphoric acid. It was of interest to discover whether protonation of the esters would take place at the terminal carbon atom of the η^4-diene system as with the ketone derivatives, or at either oxygen of the carboxymethyl group. We have studied the alkaline hydrolysis of two of the methyl ester complexes, which provides a route to the free acids.

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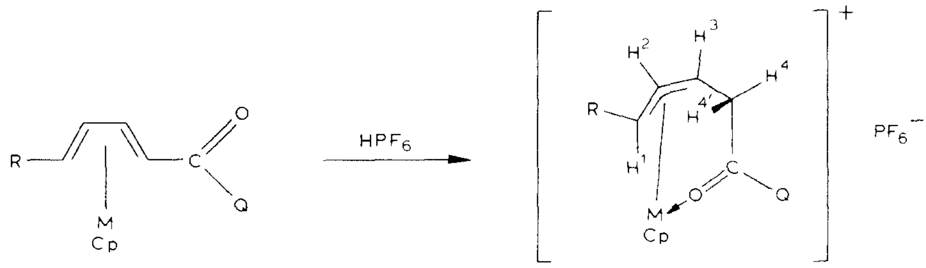
Results and discussion

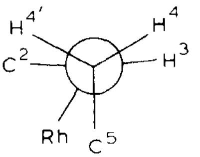
The complexes $[M(\eta^4\text{-RCH=CHCH=CHCOQ})(\eta^5\text{-C}_5H_5)]$ (I–V) on treatment with hexafluorophosphoric acid diethyl etherate in diethyl ether are converted in good yield into crystalline salts by protonation at the terminal carbon atom of the diene system adjacent to the COOMe or COMe group.



(I : M = Rh, R = Me, Q = OMe;
II : M = Ir, R = Me, Q = OMe;
III : M = Rh, R = Ph, Q = OMe;
IV : M = Rh, R = Me, Q = Me;
V : M = Ir, R = Me, Q = Me)

(VI : M = Rh, R = Me, Q = OMe;
VII : M = Ir, R = Me, Q = OMe;
VIII : M = Rh, R = Ph, Q = OMe;
IX : M = Rh, R = Me, Q = Me;
X : M = Ir, R = Me, Q = Me)

The structure of the protonated complexes VI–X is proposed on the basis of infrared and ^{1}H NMR results. The CO stretching band of the COOMe or COMe group in VI–X occurs between 70 and 80 cm^{-1} lower than in the precursors I–V (Table 3). A similar lowering in frequency has been observed on protonation of analogous diaryldienone complexes [2] and has been attributed to coordination of the $>C{=}O$ group to the metal. This coordination restricts rotation about the C^3–C^4 bond. The presence of a chiral centre at C^3 makes the two protons H^4, $H^{4'}$ of the adjacent CH_2 group magnetically inequivalent. The conformation of substituents about the C^3–C^4 bond is shown below, looking from C^4 towards C^3.



The ^{1}H NMR spectra of VI–X are given in Table 2. The large geminal coupling constant $J(H^4H^{4'})$ of ca 21 Hz and the small vicinal coupling constant $J(H^3H^{4'})$ is consistent with this conformation, as previously discussed [2,3].

Base catalysed hydrolysis of the esters I and III affords, after acidification with trifluoroacetic acid, the acid complexes $[Rh(\eta^4\text{-RCH=CHCH=CHCOOH})(C_5H_5)]$ (XI, R = Me and XII, R = Ph), respectively. Preliminary measurements of the apparent pK_a values of these acids in aqueous ethanol shows that they are about 0.4 pK unit higher than those of the free 2,4-hexadienoic and 5-phenyl-2,4-pentadienoic acids, respectively, [4]. This suggests that the $[C_5H_5Rh]$ group is weakly electron donating towards the coordinated dienoic acid.

(*Continued on p. 209*)

TABLE 1

^{1}H NMR DATA FOR THE COMPLEXES $[M(\eta^4\text{-RCH=CHCH=CHCOOZ})(\eta^5\text{-C}_5H_5)]$ [a]

Complex		Chemical shift (δ, ppm)						
	M	H^1	H^2	H^3	H^4	R	C_5H_5	Z
I	Rh	1.62(m)	4.87(m)	5.44(m)	1.26(dd) $J(H^3)$ 7.3 J(Rh) 2.3	1.42(d) $J(H^1)$ 6.3	5.12(d) J(Rh) 0.7	3.62(s)
II	Ir	0.94(m)	4.84(dd) $J(H^1)$ 6.4 $J(H^3)$ 3.7	5.31(dd) $J(H^4)$6.0 $J(H^3)$3.7	1.17(d) $J(H^3)$ 5.4	1.45(d) $J(H^1)$ 5.9	5.11(s)	3.60(s)
III	Rh	1.43(dd) $J(H^2)$ 7.4 J(Rh) 1.8	5.47(m)	5.65(m)	1.54(dd) $J(H^3)$ 7.7 J(Rh) 1.8	7.20(m) 7.12(m)	4.93(d) J(Rh) 1.4	3.66(s)
XI	Rh	1.62(m)	4.86(m)	5.39(m)	1.16(dd) $J(H^3)$ 7.3 J(Rh) 2.3	1.36(d) $J(H^1)$ 5.8	5.07(d) J(Rh) 1.0	not observed
XII	Rh	1.52(dd) $J(H^2)$ 7.3 J(Rh) 1.8	5.51(m)	5.68(m)	2.51(dd) $J(H^3)$ 8.0 J(Rh) 1.8	7.23(m) 7.13(m)	4.97(s)	not observed

[a] Measured in $CDCl_3$ relative to tetramethylsilane, $\delta = 0$ ppm. Coupling constants in Hz.

TABLE 2

^{1}H NMR DATA FOR THE COMPLEXES [M(η^3-RCH^{1}CH^{2}CH^{3}CH^{4}H$^{4'}$COQ)(η^5-C$_5$H$_5$)]$^+$ PF$_6^-$ [a]

Complex		Chemical shift (δ, ppm)							
	M	H^1	H^2	H^3	H^4	H$^{4'}$	Q	C$_5$H$_5$	R
VI	Rh	3.56(dq) J(Rh) 5.9	5.68(m)	5.27(m)	3.42(dd) J(H$^{4'}$) 20 J(H^3) 8.3	2.67(dd) J(H^4) 22.2	3.82(s)	5.60(d) J(Rh) 0.7	2.13(d) J(H^1) 6.3
VII	Ir	2.80(m)	5.80(dd) J(H^1) 11.2 J(H^3) 6.8	5.40(m)	3.47(dd) J(H$^{4'}$) 20.2 J(H^3) 8.5	2.61(dd) J(H^4) 20.2 J(H^3) 2.0	3.91(s)	5.73(s)	2.09(d) J(H^1) 5.9
VIII	Rh	4.45(d) J(H^2) 12.4	6.13(ddd) J(H^1) 12.4 J(H^3) 7.3 J(Rh) 2.3	5.92(m) J(H^4) 8.5 J(H^4) 2.3	3.56(dd) J(H^1) 20.0 J(H^3) 8.5	2.84(dd) J(H^4) 20.0 J(H^3) 2.4	3.90(s)	5.46(s)	7.58(m) 7.42(m)
IX	Rh	3.30(m)	5.29(m)	5.79(m)	3.66(dd) J(H$^{4'}$) 21.0 J(H^3) 8.1	2.98(d) J(H^4) 21	2.21(s)	5.61(d) J(Rh) 0.7	2.12(d) J(H^1) 6.2
X	Ir	2.51(m)	5.87(dd) J(H^1) 10.7 J(H^3) 6.6	5.49(m)	3.70(dd) J(H$^{4'}$) 22 J(H^3) 7.8	2.67(d) J(H^4) 22	2.30(s)	5.73(s)	2.06(d) J(H^1) 5.9

[a] Measured in CD$_3$NO$_2$ relative to tetramethylsilane, δ = 0 ppm. Coupling constants in Hz.

Experimental

Reactions were carried out under dry nitrogen. Most of the compounds described in this paper, however, appear to be stable to air both in the solid state and in solution. Microanalyses were by Butterworth Laboratories Ltd. Infrared spectra were determined in Nujol mulls using a Perkin–Elmer 257 spectrometer and were calibrated by polystyrene film. Hydrogen-1 (250 MHz) NMR spectra were recorded on a Bruker spectrometer at King's College, University of London.

5-Phenyl-2,4-pentadienoic acid (m.p. 165°C, Lit. [5] 166°C) and its methyl ester (m.p. 72°C, Lit. [5] 71°C) were obtained by the method of Hinrichsen and Triepel. (η^4-3,5-Heptadien-1-one)(cyclopentadienyl)-rhodium (IV) and -iridium (V) were prepared as previously described [6]. Some typical procedures used in the preparation of the other complexes are given below.

Preparation of (η^4-methyl-2,4-hexadienoate)(η^5-cyclopentadienyl)rhodium (I)

Dicyclooctenechlororhodium (2.0 g) was stirred with methyl 2,4-hexadienoate (4 cm^3) in petroleum ether (b.p. 40–60°C) for 1.5 h. The orange precipitate of $[RhCl(CH_3CH{=}CHCH{=}CHCOOCH_3)_2]$ [7] was filtered off, washed with petroleum ether and dried in air. Yield 1.53 g (70%); ν(CO), 1708 cm^{-1}. This product (1.50 g) was dissolved in dichloromethane (50 cm^3) under nitrogen and thallium cyclopentadienide (1.20 g) added. After stirring for 12 h in the dark precipitated thallium chloride was filtered off and the filtrate was evaporated to dryness. The oily residue was triturated with aqueous methanol (1/1 v/v) and the yellow crystals (0.75 g) filtered off. The filtrate was chilled to 0°C overnight, affording a further crop of crystals (0.20 g). Yield 0.95 g, 82% m.p. 64–65°C. The analytical sample was recrystallised from methanol as orange needles, m.p. 65°C.

Preparation of (η^4-methyl-5-phenyl-2,4-pentadienoate)(η^5-cyclopentadienyl)rhodium (III)

Dicyclooctenechlororhodium (3.0 g) and the ester (4.0 g) were stirred together in a mixture of equal volumes of diethyl ether and petroleum ether (b.p. 40–60°C) (100 cm^3) for 2 h. The deep red precipitate of $[RhCl(C_6H_5CH{=}CHCH{=}CHCOOCH_3)]_2$ was filtered off, washed with diethyl ether and dried in air. Yield 2.55 g (93%), m.p. 175–180°C (decomp.), Found: C, 44.4; H, 3.9. $C_{12}H_{12}ClO_2Rh$ calcd.: C, 44.1; H, 3.7. This product (2.50 g.) and thallium cyclopentadienide (2.30 g) were stirred in dichloromethane (100 cm^3) for 20 h in the dark. Thallium chloride was filtered off and the filtrate evaporated to dryness, leaving an orange-red oil, which crystallised on trituration with petroleum ether. The complex III was purified by recrystallisation from aqueous methanol to give orange crystals (Table 3).

Alkaline hydrolysis of III

The ester complex III (1.3 g) was heated under reflux for 8 h with potassium hydroxide (4.5 g) in water (50 cm^3) and methanol (5 cm^3). The reaction mixture was cooled to room temperature and a solution of trifluoroacetic acid (10 cm^3) in water (100 cm^3) was added. The brownish orange precipitate was filtered off, washed with water and recrystallised from aqueous methanol to give orange crystals of XII (Table 3). The sorbic acid complex, XI, was prepared similarly from I.

TABLE 3

ANALYTICAL AND SPECTROSCOPIC DATA FOR THE COMPLEXES $[M(\eta^4\text{-}RCH{=}CHCH{=}CHCOQ)(C_5H_5)]$ AND $[M(\eta^3\text{-}RCHCHCHCH_2COQ)(C_5H_5)]^+\ PF_6^-$

Complex	Colour	Yield (%)	M.p. (°C)	Analysis Found (calcd.) (%)		IR (cm^{-1})^a ν(CO)
				C	H	
I	Orange	82	64–65	49.8 (49.0)	5.3 (5.1)	1703
II	Pale yellow	52	69– 70	38.0 (37.6)	4.0 (3.9)	1710
III	Orange	76	117–118	57.3 (57.3)	5.0 (4.8)	1705
VI	Orange	97	138–140 (decomp.)	32.9 (32.8)	3.7 (3.7)	1626
VII	Cream	80	133 (decomp.)	27.1 (27.2)	3.0 (3.0)	1607
VIII	Orange red	82	140–144 (decomp.)	40.7 (40.7)	3.7 (3.6)	1625
IX	Orange	60	130–131	34.0 (34.0)	3.8 (3.8)	1632
X	Cream	68	126–127 decomp.	28.9 (28.1)	3.2 (3.1)	1615
XI	Orange	53	150–155 (decomp.)	47.2 (47.2)	4.7 (4.5)	1665
XII	Orange	58	178–182 (decomp.)	56.2 (56.2)	4.4 (4.4)	1664

[a] Nujol mull. ν(CO) for $H_3CCH{=}CHCH{=}CHCOOCH_3$ – 1710 cm^1; $H_3CCH{=}CHCH{=}CHCOCH_3$ – 1670 cm^{-1}; $C_6H_5CH{=}CHCH = CHCOOCH_3$ – 1715 cm^{-1}.

Preparation of the salts VI–X

A typical reaction is described. Compound III (0.222 g) was dissolved in diethyl ether (40 cm^3) and cooled to –70°C. $HPF_6 \cdot Et_2O$ (0.2 cm^3) was added dropwise with stirring. The reaction mixture was allowed to warm up slowly to room temperature. The orange-red crystals of VIII were filtered off, washed with ether and purified by dissolving in nitromethane, filtering and reprecipitating with ether. Yield 0.257 g (82%) (Table 3).

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