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DIENE AND DIENYL COMPLEXES OF TRANSITION ELEMENTS

IX *. FORMATION OF (1–3:5–6)η-HEXADIENYL-η^5-CYCLOPENTADIENYLRHODIUM CATIONS BY PROTONATION OF η^4-TRIENE COMPLEXES

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Summary

The triene complexes [Rh{η^4-Ph(CH)$_4$CH=CHR}(η^5-C$_5$H$_5$)] (R = H, Ph), prepared by Wittig reactions from [Rh{η^4-Ph(CH)$_4$CHO}(η^5-C$_5$H$_5$)], are protonated by trifluoroacetic acid to give the allyl-olefin cations [Rh{1–3 : 5–6-η-Ph(CH)$_3$CH$_2$CH=CHR}(η^5-C$_5$H$_5$)]$^+$ rather than the expected 1-5-η-dienyl cations.

Introduction

Protonation of tricarbonyl(η^4-hexatriene)iron complexes affords tricarbonyl(η^5-pentadienyl)iron cations [2,3]. We found recently that the complex [Rh{4–7-η-PhCOCH=CH(CH)$_4$Ph}(η^5-C$_5$H$_5$)] reacts similarly with HPF$_6$ to form an η^5-pentadienyl salt [Rh{η^5-PhCOCH$_2$(CH)$_5$Ph}(η^5-C$_5$H$_5$)]$^+$ PF$_6^-$ [4].

Accordingly the protonation of two other rhodium triene complexes, in which the triene ligand lacked the benzoyl substituent, was investigated with a view to establishing a general method for preparing the η^5-pentadienyl cations. Unexpectedly protonation took place at the terminal carbon atom of the coordinated diene which bore the vinyl substituent, rather than at the uncoordinated double bond. This resulted in the formation of an allyl-olefin (1–3 : 5–6-η-bonded) complex rather than a dienyl (1–5-η-bonded) derivative.

Results and discussion

The triene complexes (IIa, IIb) were prepared by the Wittig reaction from (η^4-5-phenyl-2,4-pentadienal)(η^5-cyclopentadienyl)rhodium(I) [4] as shown in

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* For part VIII, see ref. 1.

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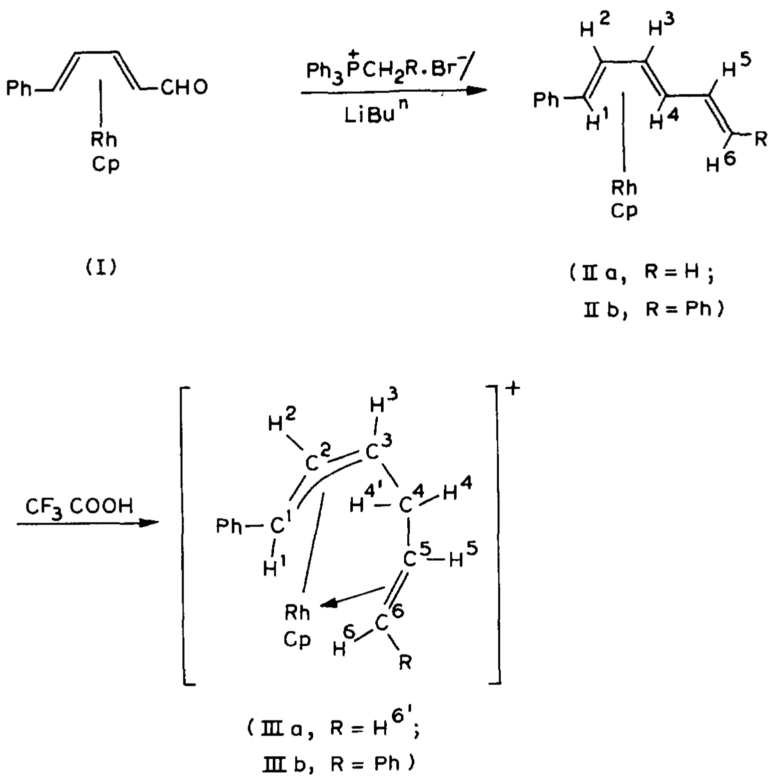
TABLE 1

^{1}H AND ^{13}C NMR DATA FOR THE COMPLEXES [a]

Complex	Chemical shift (δ, ppm)									
	H^1	H^2	H^3	H^4	$H^{4'}$	H^5	H^6	$H^{6'}$	C_5H_5	Ph
IIa	2.27(dd) $J(H^2)$7.9 J(Rh)1.9	4.97(m)	5.21(m)	2.17(m) $J(H^2,H^4) \sim 8.7$ J(Rh)1.8		5.74(m) $J(H^6)$17.0	5.17(dd) $J(H^5)$17.0 $J(H^{6'})$1.7	4.83(dd) $J(H^5)$10.2 $J(H^6)$1.7	4.88(d) J(Rh)1.0	7.03– 7.25(m)
IIb	2.38(d)	5.10(m)	5.26(m)	2.38(m)		6.21(dd) $J(H^6)$15.7 $J(H^4)$9.9	6.57(d) $J(H^6)$15.7		4.90(d) J(Rh)1.0	7.06– 7.38(m)
IIIa	3.81(d) $J(H^2)$11.7	5.76(ddd) $J(H^1)$11.6 $J(H^3)$6.7 J(Rh)1.5	4.84(q) $J \sim 7.5$	3.23(m) $J(H^{4'})$13.1	1.45(m) $J(H^4)$13.1	3.8(m)	2.90(dd) $J(H^5)$13.6 J(Rh)1.7	4.36(dd) $J(H^5)$7.8 J(Rh)1.7	5.44(s)	~ 7.4(m)
IIIb	4.49(d) J(H^2)11.6	5.67(ddd) $J(H^1)$11.6 $J(H^3)$6.7 J(Rh)1.6	5.04(q) $J \sim 7.5$	3.44(m) $J(H^{4'})$13.4	1.71(m) $J(H^4)$13.4	4.64(m)	5.33(ddd) $J(H^5)$13.4 J(Rh)1.8		4.88(d) J(Rh)0.7	7.3–7.6(m)

[a] Measured in $CDCl_3$ relative to tetramethylsilane, $\delta = 0$ ppm. Coupling constants in Hz. ^{13}C NMR spectra in $CDCl_3/CF_3COOH$ from TMS-chemical shift, J(Rh–C): Compound IIIa: 137.6, 129.8, 129.7, 129.4, 126.1 (Ph); 91.6, 5.3 Hz (C_5H_5); 81.2, 6.7 Hz (C^2); 75.0, 9.0 Hz (C^1); 59.6, 10.0 Hz (C^6); 39.8, 5.4 Hz (C^3); 39.2, 5.1 Hz (C^5); 21.7, –(C^4). Compound IIIb: 138.1, 136.7, 130.3, 130.2, 130.0, 129.8, 126.3, 126.1 (Ph); 94.6, 5.6 Hz (C_5H_5); 93.3, 7.9 Hz (C^6); 82.4, 6.6 Hz (C^2); 76.5, 9.0 Hz (C^1); 42.6, 5.2 Hz (C^3); 33.8, 5.9 Hz (C^5); 23.0, –(C^4).



SCHEME 1

Scheme 1. Complex IIb was also obtained by a standard procedure from the bis(cyclooctene)chlororhodium dimer and diphenylhexatriene, followed by treatment with thallium cyclopentadienide. The Wittig procedure is preferred as in the other method a product mixed with free diphenylhexatriene is obtained. The separation of IIb from diphenylhexatriene was achieved by column chromatography followed by recrystallisation from acetone, but with significant loss of product.

Protonation of IIa and IIb by trifluoroacetic acid in $CDCl_3$ solution was studied by ^1H and ^{13}C NMR spectroscopy (see Table 1). The ^1H spectra clearly indicate the allyl-olefin structures (IIIa, IIIb) for the protonated species. In particular the $CH^4H^{4'}$ protons, which are magnetically inequivalent, resonate at high field with a geminal coupling constant $|J(H^4,H^{4'})|$ of 13.1 Hz [5]. The question whether or not the olefinic group is bonded to the metal is solved by the ^{13}C NMR spectra. Carbon nuclei bonded to rhodium can be identified by the observation of ^{103}Rh–^{13}C coupling, usually of the order of 4–16 Hz [6,7]. Such couplings are present in the spectra of IIIa and IIIb for the five carbon atoms C^1, C^2, C^3, C^5, C^6 but not for the methylene carbon, C^4. The ^{13}C spectra were assigned by application of the DEPT * sequence to identify the CH_2 groups [8] and by selective irradiation at appropriate frequencies in the ^1H spectrum.

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* DEPT = distortionless enhancement by polarisation transfer.

Previous studies have revealed the tendency of η^4-diene complexes to undergo protonation at a terminal carbon atom of the diene system [9,10]. With a weakly coordinating acid the product will possess a 16-electron configuration, be coordinatively unsaturated and possibly labile. In some cases, therefore, the initial protonation is followed by a series of hydrogen migrations [11]. Such migrations can be suppressed or the stability of the protonated species improved if there is a donor group in the ligand which is able to coordinate intramolecularly to the metal, thus producing a coordinatively saturated system. This donor group may, for example, be $>$C=O [12,13], $>$C=C$<$ [11,14] or even an "agostic" hydrogen [15,16,17]. The results described in this paper are consistent with these other observations. Whether the $\eta^3:\eta^2$ cations described here are thermodynamically favoured over the more delocalised η^5-dienyl cations or whether they are kinetic products is not yet known. This question is being investigated further.

Experimental

Reactions were carried out under dry nitrogen. Microanalyses were by Mrs. E. Whitaker of this Department. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker WM 250 instrument at King's College, University of London.

η^4-(5-phenyl-2,4-pentadien-1-al)(η^5-cyclopentadienyl)rhodium (I) was prepared as previously described [4].

Wittig reactions of compound I

One example is described.

Benzyltriphenylphosphonium chloride (0.80 g, 2.1 mmol) suspended in dry diethyl ether (40 cm^3) was treated with n-butyllithium solution (1.4 cm^3, 1.6 *M* in hexane, 2.2 mmol), and stirred for 2 h. Complex I (0.652 g, 2 mmol) was added, the mixture stirred at room temperature overnight and then heated under reflux for 5 h. The ether was removed in vacuo and the residue washed with a methanol/water mixture (3/2 v/v), and then with a little cold methanol. Yield 0.74 g (93%). The analytical sample IIb was recrystallised from acetone, m.p. 193–194°C (dec.). Found: C, 68.96; H, 5.23. $C_{23}H_{21}Rh$ calcd.: C, 69.00; H, 5.29%.

Complex IIa was prepared similarly. Yield 93%, m.p. 122°C. Found: C, 63.69; H, 5.04. $C_{17}H_{17}Rh$ calcd.: C, 62.97; H, 5.29%.

Preparation of IIb from 1,6-diphenylhexatriene

[RhCl(cyclooctene)$_2$]$_2$ (0.352 g, 0.5 mmol) were stirred with diphenylhexatriene (232 mg, 1 mmol) in ether (50 cm^3) for 6 days. The brown precipitate was filtered off washed with ether and dried in air. Yield 0.261 g, m.p. 177–181°C (dec.). Elemental analysis varied from sample to sample. This brown product (0.55 g) was stirred overnight with thallium cyclopentadienide (0.45 g) in dichloromethane (50 cm^3). Thallium chloride was filtered off and the filtrate evaporated to dryness leaving an orange-brown solid. This was washed with petroleum ether, dissolved in a little benzene and chromatographed on silica gel using 20% benzene + 1% triethylamine in cyclohexane as eluant. An orange band eluted which afforded an orange solid (0.230 g), shown to be a mixture of IIb and diphenylhexatriene by infrared analysis. Two recrystallisations from acetone removed the latter impurity. Yield 84 mg, m.p. 193–195°C (dec.). Found: C, 68.43; H, 5.18: $C_{17}H_{17}Rh$ calcd.: C, 69.00; H, 5.29%.

Protonation studies

Trifluoroacetic acid was added to a solution of the complex in $CDCl_3$ at −70°C in an NMR tube. The sample was allowed to warm to ambient temperature before the spectrum was recorded.

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References

1 M.A. Paz-Sandoval, P. Powell, M.G.B. Drew and R.N. Perutz, Organometallics, submitted for publication.

2 H.J. Dauben and D.J. Bertelli, J. Amer. Chem. Soc., 83 (1961) 497; R. Burton, L. Pratt and G. Wilkinson, J. Chem. Soc., (1961) 594.

3 P. McArdle and H. Sherlock, J. Chem. Soc., Dalton Trans., (1978) 1678.

4 P. Powell, J. Organomet. Chem., 244 (1983) 393.

5 D.H. Williams and I. Fleming, Spectroscopic Methods in Organic Chemistry, McGraw Hill, London, 2nd ed., 1973, p.111.

6 B.E. Mann and B.F. Taylor, ^{13}C NMR Data for Organometallic Compounds, Academic Press, London, 1981.

7 P.W. Clark and A.J. Jones, J. Organomet. Chem., 122 (1976) C41.

8 R.K. Harris, Nuclear Magnetic Resonance Spectroscopy, Pitman, London, 1983, p.175.

9 P. Powell in F.R. Hartley and S. Patai (Eds.), The Chemistry of the Metal–Carbon Bond, Wiley, New York, 1982, Chapter 8.

10 L.A. Oro, Inorg. Chim. Acta, 21 (1977) L6.

11 B.F.G. Johnson, J. Lewis and D.J. Yarrow, J. Chem. Soc., Dalton Trans., (1974) 1054.

12 P. Powell, J. Organomet. Chem., 206 (1981) 229.

13 P. Powell, J. Organomet. Chem., 243 (1983) 205.

14 L.A. Oro, J. Less Common Metals, 53 (1977) 289.

15 M. Brookhart and M.L.H. Green, J. Organomet. Chem., 250 (1983) 395.

16 M. Brookhart, W. Lamanna and A.R. Pinhas, Organometallics, 2 (1983) 638.

17 J.M. Williams, R.K. Brown, A.J. Schultz, S.D. Stucky and S.D. Ittel, J. Amer. Chem. Soc., 100 (1978) 7407.